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EVALUATION OF SAMPLE COLLECTION AND ANALYSIS TECHNIQUES FOR ENVIRONMENTAL PLUTONIUM

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Soil is the primary reservoir for plutonium in the environment but inhalation, with the resulting lung dose, is the primary pathway for human exposure. This evaluation is therefore primarily oriented toward sampling and analysis of soil and air, with secondary consideration of other environmental media.

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David E. Bernhardt

May 1976

OFFICE OF RADIATION PROGRAMS - LAS VEGAS FACILITY
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This report has been reviewed by the Office of Radiation Programs - Las Vegas Facility, Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

The Office of Radiation Programs of the U.S. Environmental Protection Agency carries out a national program designed to evaluate population exposure to ionizing and non-ionizing radiation, and to promote development of controls necessary to protect the public health and safety. This literature survey was undertaken to assess the available information concerning sampling and analysis techniques for environmental concentrations of plutonium. Readers of this report are encouraged to inform the Office of Radiation Programs of any omissions or errors. Comments or requests for further information are also invited.

Donald W H.

Donald W. Hendricks
Director, Office of
Radiation Programs, LVF

EVALUATION OF SAMPLE COLLECTION AND ANALYSIS TECHNIQUES FOR ENVIRONMENTAL PLUTONIUM

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Information concerning sampling and analysis techniques for plutonium in the environment is presented and evaluated in this report. Consideration is given to available techniques and their applicability to various situations, sensitivities of the techniques, and the validity and reproducibility of results.

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The author, although recognizing the assistance of many people, accepts full responsibility for the content of this report.

INTRODUCTION

OBJECTIVE

The objective of this report is to review and evaluate past, present, and proposed environmental sample collection and analysis techniques for the measurement of plutonium and associated transuranic elements. Consideration is given to the various available techniques, their applicability to various situations, sensitivities of the techniques, and reproducibility of results.

Soil sampling appears to be the predominant technique for assessing accumulative environmental levels of plutonium (AEC, 1974). Thus, emphasis in this review has been placed on soil sampling and analysis, although consideration is given to other media, especially air sampling. Air sampling is emphasized because of the predominance of the inhalation pathway for plutonium. The review is largely based on published information from nationally recognized laboratories, although some unpublished data, which may include unintentional bias, is included.

GENERAL STATUS OF TECHNIQUES AND THEIR EVALUATION

There are several published intralaboratory evaluations of analytical techniques (e.g. Chu, 1971; Bishop et al., 1971; Sill, 1971; Sill and Hindman, 1974). There are also several reports containing limited data from interlaboratory comparisons (Krey and Hardy, 1970; AEC, 1973; Sill and Hindman, 1974). These studies have largely dealt solely with analytical techniques for soil samples, with limited consideration of the interaction between sample collection and analytical techniques. Krey and Hardy (1970) and Bliss (1973) present some data on the interaction of both collection and analysis, but there does not appear to be any comprehensive evaluation of both collection and analytical techniques.

Most analytical cross-check programs intra- or interlaboratory are done with samples containing plutonium concentrations significantly above background (roughly 0.05 pCi/g of dry soil for a 5 cm depth sample). But, there are several limited groups of data available for replicate analyses of samples containing near-background plutonium levels. These are reported by Sill (1971), AEC (1973), Krey and Hardy (1970), and Butler et al. (1971).

Much of the difficulty with the sampling and analysis of soil samples appears to relate to the discrete particulate nature of plutonium contamination under some circumstances. The potential refractory nature of plutonium, along with the potential for producing refractory material during sample preparation aggravates the inherent difficulties and complexities of the analysis (Sill, 1971; and Sill and Hindman, 1974).

Although there are considerable variations and potential inadequacies in past techniques, and to a lesser extent in current techniques, there is cause for optimism for improvements, or at least standardization, in the near future. In May 1974, the Atomic Energy Commission (now Nuclear Regulatory Commission-NRC) issued Regulatory Guide 4.5, "Measurements of Radionuclides in the Environment, Sampling and Analysis of Plutonium in Soil" (AEC, 1974). This Guide outlined generally compatible and supplementary collection and analysis techniques. In April 1974, the Environmental Protection Agency (EPA), National Environmental Research Center-Las Vegas (NERC-LV; now known as Environmental Monitoring and Support Laboratory, EMSL) sponsored a workshop on soil collection and analysis techniques. A summary of this workshop (attached as Appendix A) and the tentative reference method developed from it (Bretthauer et al., 1975) were issued in 1975.

The following paragraphs are extracted from the EPA criteria for standard methods (EPA, 1973).

"Sampling is the removal from the environmental continuum of a portion of the pollutant for detailed investigation. Sampling involves containerizing a discrete volume of polluted air, water, soil, or biological materials, or it may involve partitioning the pollutant directly from these media into a filtering or absorbing device or into another fluid (e.g., the absorption of the sulfur dioxide pollutant in air into a solution of potassium tetrachloromercurate). Additionally, it includes those procedures necessary to preserve the sample. In all of these sampling methods, we must accurately know what fraction of the pollutant passes from the environmental continuum into the sample. Standardization of the sampling method establishes the reproducibility of this relationship. This relationship must be shown to be stable or to follow predictable changes from the time the sample is taken to the time the sample is worked up for analysis."

"Sample work-up consists of the preparation of the sample by concentration of pollutant, removal of interfering substances, etc., for the analytical procedures to follow. It must be established that all pollutant losses during sample work-up can be quantitatively accounted for and are reproducible within statistically acceptable limits."

"Analytical methods are designed to give accurate estimates of the true amount of pollutant remaining in the worked-up sample. The standardization procedure assures that these values are reproducible within statistically-acceptable limits. The value derived from the analytical method adjusted for predictable losses in sampling and sample work-up gives the estimation of the true concentration of the pollutant in the environmental continuum."

"The reference method is the best, readily available method. Under most circumstances, it will be expected that the reference method will be the method of choice of most user laboratories. When other methods must be used for any reason, their equivalence to the performance characteristics of the reference method must be demonstrated to assure that data generated by their use is equivalent to that generated by the reference method and that statistically valid comparisons can be made between such data and that generated by use of the reference method."

EPA started a standards distribution program for plutonium-239 and americium-241 in December 1973 (EPA, 1974a). A plutonium-239 cross-check program for water samples (<10 pCi/1) was initiated in 1974 (EPA, 1974b).

A basic problem in most environmental monitoring programs is inadequate coordination of the sampling and analytical programs. This is exemplified by a field program where significant efforts are made to obtain unbiased soil samples representative of the sampled area. This sample may represent kilograms of material. The analyst, in order to insure complete dissolution of the material, analyzes a one- or possibly ten-gram aliquot of this sample. If the plutonium contaminant is of a discrete particulate nature, replicates from this sample can vary by several orders of magnitude (Bliss, 1973). Therefore, the objectives of the monitoring program must be continually examined and reevaluated.

DIRECT FIELD MEASUREMENT TECHNIQUES

The most viable means of field measurement for plutonium contamination appears to be the FIDLER (Field Instrument for Detecting Low Energy Radiation) instrument developed by the Lawrence Livermore Laboratory (Tinney et al., (1969). The FIDLER uses a thin NaI or CaF crystal (Piltingsrud and Farr (1973)) and photon pulse height discrimination to detect the 17-keV X-rays from the progeny of plutonium, or the 60-keV gamma photon of americium-241. Although the sensitivity of the FIDLER instrument, ideally about 130 nCi/m^2, is about two orders of magnitude above ambient background levels of plutonium (nominally 1-2 nCi/m^2 of plutonium-239, it provides significantly greater utility for contamination surveys than the prior alpha detection survey instruments.

Minimum sensitivities or calibration factors in terms of pCi/m^2 are generally not stated for most alpha survey meters (Dummer, 1958). Survey instruments are generally only designed for assessing the relative degree of contamination. Information from general sources, including Dummer (1958) indicates a general sensitivity, under ideal field conditions, of about 5-10 pCi/cm^2 (50-100 nCi/m^2). The response relationship is about 500 cpm per 100 nCi/m^2. However, these relationships assume that the alpha activity is essentially emitted from an infinitely thin layer of contamination on a smooth surface. Further, the measurement is made with a fragile mylar-windowed probe, which must essentially be placed in contact with the surface. A layer of moisture (dew) essentially will shield out the alpha particles. There are problems of fracturing or contaminating the probe. Vegetation or rocks make it very difficult to place the probe near the surface. Measurements taken at one centimeter from the surface are in error by roughly a factor of two (Dummer, 1958).

Table 1 presents sensitivities and calibration factors for the FIDLER instrument. These values are based on a nominal background of 200 cpm for the 17-keV region and 600 cpm for the 60-keV region. These values assume the background is known within counting error variations. The 17-keV sensitivities relate to a net background counting rate of 75 cpm, above the background of 200 cpm. Thus, an uncertainty in background of 100 cpm, which is possible assuming the background was determined in a distant contamination-free area, introduces a factor of two error.

TABLE 1. SENSITIVITIES AND CALIBRATION FACTORS FOR FIDLER INSTRUMENTS

(1/16" NaI(Tl) crystal)

Nuclide	Energy Region (KeV)	Minimum Sensitivity (nCi/m^2)	Response ($cpm/nCi/m^2$)	Minimum Sensitivity Point Source (nCi)
Plutonium-238	17	56	1.3	28
Plutonium-239	17	130	0.58	63
Americium-241	17	19	3.9	9.4
Americium-241	60	36	36	19
100% photon	17	7	10.1	3.6
100% photon	60	13	100	6.9

Lindeken et al. (1971) studied the background in the 17-to 60-keV energy region. He concluded that although the background may vary by a factor of two in adjacent areas, the energy spectral shape, or the percentage of the background per 10-keV interval, varied by less than 5 percent. Thus, in the absence of general fission product gamma fluxes, the background at about 60 keV (Compton continuum) can be measured within an area of suspected plutonium contamination, and the background in the 17- and 60-keV regions estimated. This technique can be used to supplement or replace other background readings, to minimize the errors associated with variations in background.

Piltingsrud and Farr (1973) report on a modified FIDLER-type instrument using a CaF(Eu) crystal. The modified instrument is amenable for field repair and costs less than the NaI(Tl)-type instrument. A sensitivity value of about twice that for the NaI(Tl) instrument is reported.

Tinney et al. (1969) report field tests for the NaI(Tl)-type FIDLER at the Nevada Test Site. They estimated the actual background to be 400 counts/min, with a corresponding sensitivity of about 300 nCi/m^2. It was noted that although alpha survey instruments indicated a higher count-rate for selected point sources, it was necessary to use the FIDLER to find these sources. Furthermore, this field test indicated that for general contaminated areas, the FIDLER cpm readings were roughly ten times the alpha instrument readings, versus the theoretical ratio of about

0.1. This indicates the poor efficiency of alpha monitoring in the field (actual versus theoretical).

REECO reported (NAEG, 1971) that at NTS, with a depth-dispersed source of plutonium-239, most of the 17-keV X-rays were absorbed in the soil. Even using the americium-241 60-keV photon required a correction factor of three. The use of the FIDLER with a multichannel analyzer readout was also suggested for areas with general fission product contamination.

Gilbert and Eberhardt (1974) present data for plutonium-239: americium-241 ratios based on laboratory analysis for both nuclides, and on plutonium-239 laboratory analysis versus FIDLER estimates for americium-241 from NTS. The data are summarized in Table 2, taken from Gilbert and Eberhardt. The data indicate a change in the plutonium-239:americium-241 ratio by isopleth. The isopleths were relative concentration lines determined by FIDLER surveys. Except for the Clean Slate I and II sites, there is good correlation between the plutonium and americium ratios within the isopleths.

The ratios and correlation of the plutonium-239 to americium-241 60-keV FIDLER readings are also given in Table 2. Although the correlation improves with an increase in plutonium concentration, the correlation indicates there is little direct relationship. Figure 1 presents scatter diagrams of the plutonium-239 versus americium FIDLER data.

Although the FIDLER is an effective instrument for mapping general areas of contamination, its use as an accurate predictor of plutonium concentrations in surface soils appears to be limited, based on the NTS situation. Additonal field evaluations are necessary for a more specific conclusion.

Stuart of EG and G reports (1971) the use of gamma spectroscopy from an aerial platform for measurement of americium-241 in soil.

Due to the disagreement between published values of half-lives, and X-ray and photon yields for plutonium and americium, various values are summarized in Appendix B.

In summary, although the minimum sensitivity for the FIDLER is indicated as 130 nCi/m^2 for plutonium-239, this relates to only 75 cpm above minimum background values of 200 cpm. Given the variability in background with values up to 400 cpm, or more, extreme care has to be exercised to accurately assess net contamination at 200 or even 500 nCi/m^2. Without an accurate knowledge of background, values at these levels would have uncertainties approaching 50-100 percent. The data in Table 2 and Figure 1 indicate that even at 100 dpm/g (roughly 50 pCi/g or 500 nCi/m^2), there is limited correlation between the FIDLER results and plutonium-239 radiochemistry results. Use of the 60 keV gamma

TABLE 2. ESTIMATED CORRELATIONS BETWEEN LABORATORY GAMMA SCANS FOR AM-241 AND PU-239-240, AND BETWEEN FIDLER CPM OF AM-241 AND PU-239-240

(from Gilbert and Eberhardt, 1974)

		Lab Gamma Scans for Am-241 vs Pu-239-240			FIDLER vs Pu-239-240	
	Isopleth	No. of Samples	Estimated Correlation	Average Pu/Am Ratio ± S.E. †††	No. of Samples	Estimated Correlation
Area 13	1 < 1000 cpm	24	0.98	12.6 ± 0.9	20	0.19†
	2 1-5,000 cpm	28	0.85	14.2 ± 3.9	28	0.33††
	3 5-10,000 cpm	15	0.98	9.4 ± 0.4	14	0.51††
	4 10-25,000 cpm	20	0.99	8.8 ± 0.2	15	0.40††
	5 25-50,000 cpm	20	0.99	8.8 ± 0.3	20	0.69††
	6 > 50,000 cpm	46	0.95	9.4 ± 0.3	46	0.69††
Area 5	1	24	0.93	11.9 ± 1.0	45	0.54†
	5	10	0.99	10.9 ± 0.6	15	0.76†
TTR	Clean Slate I	10	0.73	31.7 ± 5.6	--	----
	Clean Slate II	9	0.54	37.0 ± 10.8	--	----
	Clean Slate III	22	0.91	21.7 ± 2.2	--	----
	Double Track	8	0.99	28.7 ± 1.4	--	----

†FIDLER 60-kev readings not corrected for background (correcting often resulted in negative readings).

††FIDLER 60-kev readings corrected for background.

†††These are appropriate only if the Pu/Am ratio remains constant as the Am Value varies. See text for further comments.

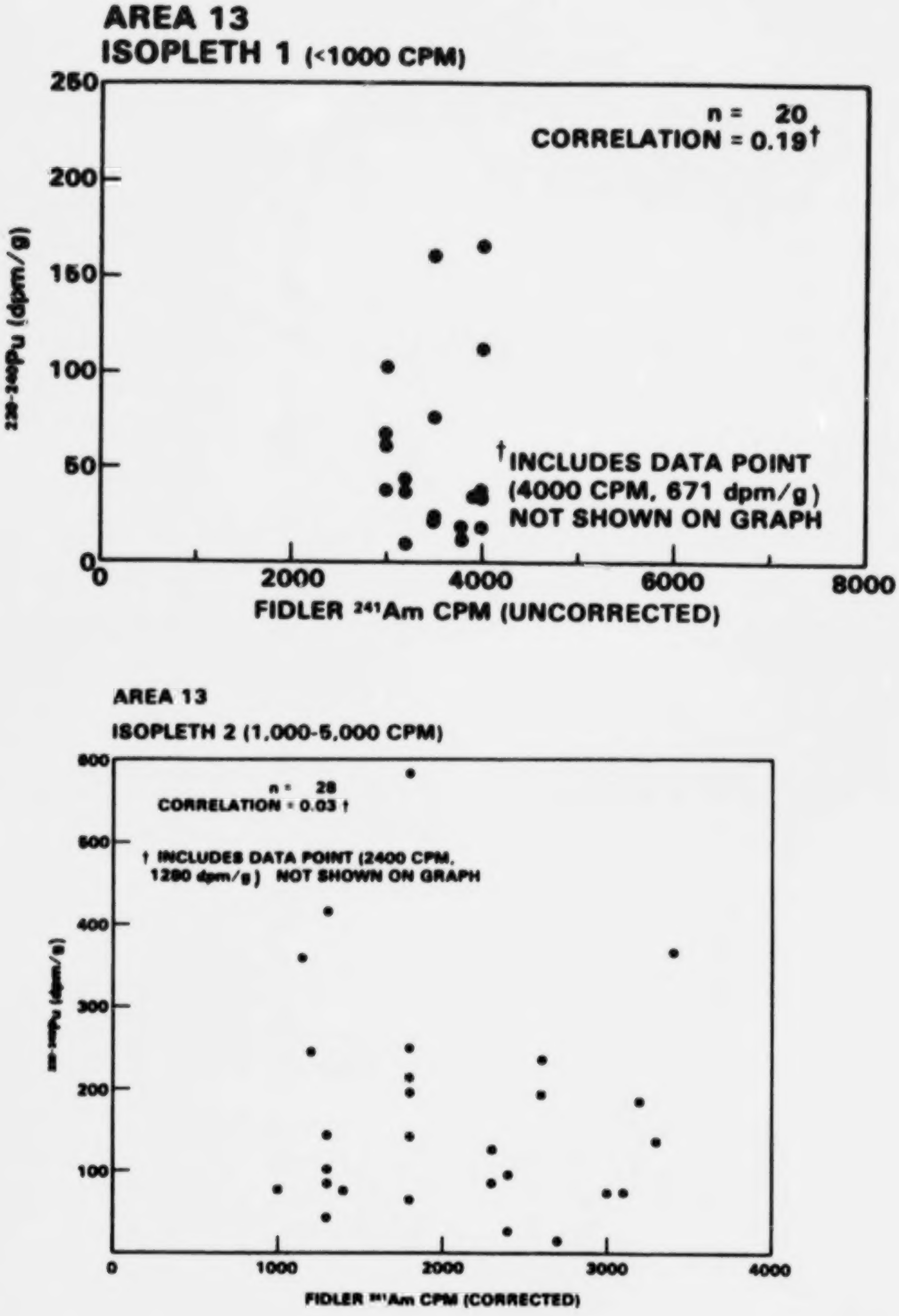

Figure 1. Correlation between Plutonium concentrations and FIDLER readings. (from Gilbert and Eberhardt,1974)

from americium-241 for field measurements is not recommended where the age of the material and the original percentage of plutonium-241 is not known.

FIELD COLLECTION TECHNIQUES FOR SOIL

The sampling or program mission and intended use of the sample results is of utmost concern in defining the adequacy of sampling techniques. The efforts and costs associated with sampling as well as the costs of analyzing unnecessary samples make it expedient to relate sampling techniques to the intended use of the data. Table 3 presents approximate costs for sample collection and analysis. The values for collection include nominal driving times between sampling sites.

TABLE 3. APPROXIMATE COSTS FOR SOIL SAMPLE COLLECTION AND ANALYSIS

	Cost	Man-hours per Sample
Sample Collection		
Surface Sample	$10-20	1
Depth Profile (3 to 5 samples)	25-50	2
Plutonium Analysis		
1 gram by Dissolution	100.00	2
10 gram by Dissolution	100.00	4-5
10 gram by Fusion Tech.	150.00	---

There are three primary considerations in sample collection:

1. Selection of the general area to be sampled; e.g., undisturbed, type and amount of vegetation, size of rocks, etc.
2. Determination of sample depth.
3. Compositing material from an adequate sample area.

Appendix A, the summary report from the NERC-LV workshop, includes an extensive discussion of sampling techniques and necessary considerations. AEC (1974) also discusses the criteria.

The intent of sampling programs can generally be related to one or more of five specific objectives:

1. Sampling for low levels, such as those associated with world-wide fallout, to establish base line or background concentrations. The deposition of the contaminant is generally fairly uniform.
2. Sampling to determine the occurrence of a release associated with a specific facility, or accident at a specific location. The deposition levels and distribution may vary with direction and distance from the point of release (Sill, 1971). This includes determining the inventory.
3. Sampling to determine the deposition during various chronological periods of time. The objectives would relate to surface samples or possibly samples from various depths that had been covered at a specific point in time.
4. Profile sampling to determine movement of material through the vertical profile. The sampling technique would be similar to general profile sampling, but samples should not be composited and depths should correspond to the soil horizons.
5. Sampling to determine quantities of source material readily available for resuspension; i.e., normally the surface one-eighth to one-half inch of soil.

Common sampling techniques are not oriented to resuspension. Thus, pertinent comments and techniques are discussed in the next section.

The required accuracy and sensitivity in conjunction with the analytical sensitivity of results must also be considered prior to selecting the sample collection techniques; e.g., dilution of the plutonium concentration in the surface layer by soil with a lower plutonium concentration from deeper profiles. The surface area represented by a sample and the allocation or splitting techniques used to select the final aliquot that is to be analyzed must be such as to meet the necessary resolution between the results based on the sampling mission objectives. Furthermore, the sampling parameters (depth and area) must be such as to give reproducible results. Michels (1971), in an analysis of data from around the Rocky Flats Plant concludes that Poet and Martell's (1972) sampling techniques probably introduced artificial variability in their results due to inadequate sampling depth. This made it difficult to differentiate between plant and world-wide contamination.

SOIL SAMPLING TECHNIQUES

The two basic techniques are presented in AEC (1974). The techniques are generally referenced to by their developers as the HASL and NAEG techniques.* They have similar philosophies, and generally are supplementary in that they are applicable for different soil types. The site selection criteria, outlined below, are similar for both techniques:

1. Select general sample locations based either on general areas around a site, average geographical distribution, or on a random basis (random numbers referenced to a geographical grid).
2. Pick undisturbed sites for actual sampling. This may require abandoning certain sites if the selection of general location is based on random numbers. Although usually unacceptable, disturbed sites, blow sand, dams, or recent landfill may be appropriate for certain mission objectives.
3. Pick open, generally flat areas where there are no nearby potential anomalies, such as near buildings or trees. Also avoid stream beds, dry wash bottoms, and hillsides.
4. Pick areas away from rock outcrops and with generally uniform vegetation coverage. Try to insure that the soil grain size is compatible with the sampling method.
5. Soil having high earthworm activity should be avoided due to the abnormally high vertical mixing.
6. Locations should be roughly 120 m (400 ft) or more from dusty roads or sites of previous construction.

The following items outline the HASL technique:

Surface Sample

1. Obtain surface samples by core technique. Any type of sampling tool that can remove an intact plug (cookie cutter-type instrument) is appropriate.
2. The surface sample depth should be 5 cm (2 inches). The sample area should be 500 to 1,000 cm^2 (about 0.5 to 1 ft^2). In grass areas the vegetation should be close-clipped and taken as a vegetation sample or discarded.

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*Energy Research and Development Agency, Health and Safety Laboratory, and Nevada Applied Ecology Group.

3. It is suggested that the sample be composed of about 10 plugs from a 5-meter line transect. The line should be located by reference to fixed landmarks.

4. The soil sampler should be pressed into the ground without twisting or disturbing the grass cover or soil surface.

5. The 5-cm depth is intended to include the soil of maximum plutonium activity and most of the root mat in areas covered with grass. In areas with a deeper root mat, it may be necessary to take a deeper surface sample to allow accurate estimation of the sample depth.

Depth Profile

1. A 3.5-in. diameter auger may be used to take incremental depth profile samples at the same locations where the surface plug was removed. Ten cores should be composited for a profile. The purpose of the profile determines the number of profiles that should be taken at a given location. Both the HASL and NAEG techniques recommend compositing a number of profiles (e.g., 10), but specific study objectives, such as determination of the movement of plutonium through the soil column, are best based on individual samples.

2. For the trench-type method, the vegetation, if present, is closely clipped, and the sod layer removed from the proposed trench area. A trench approximately 60 x 90 cm, and 60 cm deep is dug adjacent to the clipped area.

3. A rectangular three-sided 15x15x5-cm deep pan is used to take samples from the vertical wall of the trench.

4. A flat-bladed knife should be used to score the soil around the edges of the pan to allow removal of a sample having an accurate area.

5. The soil is removed from each side of the sampled area to provide a flat shelf prior to each 5 cm depth sampling increment.

6. The minimum profile depth should be based on analysis of preliminary samples (roughly a minimum of 20 cm).

7. The sampling area for this type of profile is only 230 cm^2, which provides a less representative deposition sample than does the surface sampling technique.

Sample Preparation

1. Spread out and air dry sample for about 3 days.
2. Break up soil aggregates, and pull apart and cut up root mat.
3. Weigh the total sample.
4. Remove and discard rocks greater than about 2.5 cm diameter.
5. For gravelly soil, sieve through 10 mesh, removing material greater than 2 mm.
6. Crush and blend sample.
7. Spread sample and quarter. Take a three-kilogram composite by taking small repetitive aliquots from each quarter.
8. Pulverize or grind this subsample.

The following items outline the Nevada Applied Ecology Group sampling technique. It is intended for sandy and rocky soils which cannot be sampled by core techniques.

Ring Method for Surface Samples

This technique can be used to collect either surface or profile samples.

1. A 12.7 cm-ID x 2.5 cm-deep ring is pressed into the soil.
2. The soil inside the ring is removed with a disposable plastic spoon.
3. The soil from the outside of the ring is removed, and the ring is pressed down for another sample.
4. A surface sample is defined as a minimum depth of 5 cm.
5. A minimum number of five separate samples should be taken along a straight line transect and composited for analysis.
6. The location of the transect should be related to fixed landmarks.

Trench Technique for Profiles

This method is similar to the HASL trench technique.

1. Dig trench of convenient size, 15 to 25 cm deeper than desired sampling depth.
2. Take samples from trench wall with three-sided rectangular tray (10 x 10 x 2.5 cm deep).
3. Push the tray into the trench wall. Use a flat trowel to close the open end of the tray.
4. Remove the soil around the tray down to the sampling depth. Remove the sample.
5. A sample consists of soil taken from a minimum depth of 5 cm.
6. A minimum of five samples should be taken from separate trenches along a straight line transect. Composite the samples for analysis. (Note: Most groups only take 2 samples).

General Comments

1. Samples should either be double bagged or placed in cans.
2. Varying soil types require modification - Rocky soils may require larger samples to minimize the errors associated with sampling accurate areas and depths.
3. Locations should be identified by reference to fixed landmarks.
4. Adding moisture (as a fine spray) to the soil may minimize sampling problems.

Sample Preparation

1. Oven dry soil for 24 hr at 100°C. Weigh total sample.
2. Sieve sample to remove material greater than 0.6 cm. (0.25 in.) diameter (1/4-in sieve). This excludes rocks and most root material from further consideration.
3. Rocks can be acid washed, with the wash solution added to the solubilized soil sample.
4. Roots and vegetative material can be analyzed separately.
5. The sample should be ground (ball-milled) and blended prior to taking a representative aliquot for analysis.

Table 4 summarizes collection techniques used by several investigators.

The following points emphasize the similarities of the various techniques and potential pitfalls:

1. Both the HASL and NAEG techniques have standardized on a minimum depth for surface samples of 5 cm (2 in). For most locations and situations the majority of the plutonium is in the top 3 to 5 cm. A sample representing a depth of less than 5 cm may not account for the majority of the plutonium deposition (Krey and Hardy, 1970). Furthermore, the fractional uncertainty in the sampled depth is proportional to the sampled depth (e.g., a 1-cm uncertainty is 100% of 1 cm, but only 20% of 5 cm). An unnecessarily large depth results in diluting the higher surface concentrations with (usually) relatively uncontaminated soil. This increases the uncertainty in sample results. Mixing of surface soil with subsoil can also result in a significant scatter or variance in results, if uniform methods are not used.

2. AEC (1974) emphasized that when sampling rocky soils, modified techniques may be necessary. However, a representative depth is more important than a representative width. But as Bliss (1973) notes, the measurement of the cross-sectional area is more important than the measurement of the depth, because of the direct dependence of the deposition calculations on the area represented by the sample.

3. The HASL and NAEG techniques emphasize the compositing of a number (five) of small-area samples for a given site to obtain a representative sample and a minimum sampled area (0.5-1 ft^2). This is not emphasized in many of the techniques in Table 4. In fact, as noted in Table 4, Bliss (1973) only composites two samples per horizon in depth profile samples. Bliss (verbal communication) indicated that REECO usually only takes one sample per horizon. Moore, Office of Radiation Programs - Las Vegas Facility (ORP-LVF) (verbal communication) noted that probably only one sample per horizon was taken for Enewetak.

Several potential uncertainties are associated with sample preparation. These include:

1. Oven drying at 120°C versus air drying for several days. The differences in the resulting weights (up to roughly 10 percent) are present in the pCi/g values, but should be accounted for in the pCi/m^2 values.

TABLE 4. SAMPLE COLLECTION TECHNIQUES
(Blanks indicate no information)

		SURFACE SAMPLES								PROFILE SAMPLES							
Reference	Organization	Technique	Sample Area (cm²)	(in²)	Number of Composites	Total Area (cm²)	(in²)	Sampled Depth (cm)	(in)	Technique	Increments (cm)	Area Per Sample (cm²)	(in²)	Number of Composites	Total Area (cm²)	(in²)	Sieve Size (cm)
AEC Guide (1974)	HASL	Core/Auger	60		10	600		5		Auger	0-30 total	62		10	600		<2.56
AEC Guide (1974)	HASL									Trench/Tray		225		1	225		<2.5
AEC Guide (1974)	NAEG	Ring	127		5	600		5		Trench/Tray	2.5-5	100		5	500		<0.2
AEC Guide (1974)	NAEG	Tray	100		5	500		5									<0.2
Bliss (1973)	NERC-LV/NAEG	Tray	100		10	1000		5		Trench/Tray	2.5-5	100		2	200		<0.2
Douglas (ORP-LVF)	ORP-LVF	Tray	100		10	1000		5		Trench/Tray	2.5-5	100		2	200		
Bliss (Verbal)	REECo/NAEG	Ring	127		≈1	127		5		Trench/Tray		≈100		≈1	≈100		
AEC (1973)	Enewetak	Core	30 or 60		1 or 2	30 or 60		5 or 15		Trench/Tray	≈5	100		1	100		
Corley, et al (1971)	Hanford	Shovel	549	216				1.3	0.5								
Corley, et al (1971)	Hanford	Tape Cont.	64		≈1	≤100		1.6									
Kahn, 10/1/74	EPA/NEF Cinn.							2.5	1								
Little (1973)	Colorado State University	Trench	25		4	100		3		Trench	3-21	25		4	100		
Poet & Martell (1974)		Spatula	1000		1	1000		1			0-0.3, 1.3, 2.5 ...	≈1000		1	≈1000		<.05
McClendon (1975)	SRP	Core	45		10	450		15		Core	0-5, 5-15, 15-22.5-30	45		10	450		
Krey & Hardy (1970)	HASL	Auger/Core	62		10	62		20		Auger/Core	0-5, 5-20	62		10	600		
Krey & Hardy (1970)	HASL	Template	930	144	1	930	144	20									
WASH-1259 (AEC, 1973)	LASL	Core	44		5	220		5									
WASH-1259 (AEC, 1973)	SRP	Core	62(?)		10	600(?)		5		Auger	0-5, 5-15, 15-22.5-30			10	600		
WASH-1259 (AEC, 1973)	Mound	Core	62		10	600		30.5	12								
WASH-1259 (AEC, 1973)	Mound	Scrape						0.3	1/8								
WASH-1259 (AEC, 1973)	Pantex	Core	62		≈1	≈62		5.1									
WASH-1259 (AEC, 1973)	Rocky Flats	Core	100		1	100		5									
WASH-1259 (AEC, 1973)	Sandia, Abq.	?	230	144	1	230	144	2.5	1								
WASH-1259 (AEC, 1973)	Argonne	Core	87		2	173		30									
WASH-1259 (AEC, 1973)	Idaho, NRTS	Core	79		5	390		5									
WASH-1259 (AEC, 1973)	ORNL	Core	46	7	9	410		1									
WASH-1259 (AEC, 1973)	Hanford							2.54	1								
WASH-1259 (AEC, 1973)	LLL							1;up to 25									

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2. AEC (1974) refers to calculating field bulk density. This apparently is an error in semantics because the actual field weight is not obtained. Also, standard soil sampling methods are not used to determine the volume of hole from which the sample was taken.

POTENTIAL SAMPLING ERRORS

The available literature indicates that very few efforts have been made to evaluate the adequacy of soil sampling techniques. The following subjects will be treated in this section: consideration of apparent inconsistencies in results based on calculated bulk densities; consideration of plutonium depth profiles; discrete particles; and comparision of actual analytical variations in several groups of results.

Bulk Density

Kaufmann (internal memorandum dated October 3, 1974, ORP-LVF)*, noted that the tray/trench method was probably not adequate for obtaining an accurate estimate of sample weight per sampled area. This corresponds with a preliminary workup of data by Douglas (ORP-LVF, unpublished data) for the 1973 Trinity Field Study. Figure 2 shows a histogram of weight per unit area sampled and calculated bulk densities (g/cm^2). Histograms of other samples from this study indicate similar distributions. The maximum observed values from the Trinity study are equal to the minimum bulk density indicated by Terzaghi and Peck (1968) for uniform loose sand (1.43 g/cm^3). The median values indicated by Douglas for Trinity are roughly 30 percent lower than the value indicated by Terzaghi and Peck. Bliss (verbal communication) also indicated that values of less than 1 g/cm^3 have been noted in the Nevada Test Site (NTS) EMSL work.

Kaufmann (verbal communication) indicated that although valid values of about 1 g/cm^3 are not impossible, they are improbable. In nature they result largely from undisturbed drying of a saturated soil, forming an unconsolidated matrix-like material.

The American Society of Testing Materials soil sampling method D-1556 (ASTM, 1964) specifies a minimum sample size of 1400 cm^3 for soils with a maximum particle size of 12.5 mm or 0.5 inch diameter. Furthermore, the standard specifies a technique for measuring the sample volume by refilling the sampled hole with a measured weight of sand of known density.

The methods of Bliss (1973) and Douglas, which basically follow the NAEG technique, only collect about 1,000 cm^3 per horizon for profile samples--actually only 250-500 cm^3 per sampling cut. Furthermore, the use of the tray disturbs the actual sample and the surrounding area. Also, Bliss (verbal communication) notes that the two samples for profiles (NTS) are usually taken immediately adjacent to each other. Thus, the soil disturbed by the first cut is sampled in the next cut. Also, one side of the tray is not confined by soil during the second cut.

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*ORP-LVF, Office of Radiation Programs, Las Vegas Facility

There would appear to be inaccuracies in the application of the NAEG (and other) methods. The significance of these is hard to assess, but could amount to 30 percent or more.

Inaccurate bulk densities do not necessarily affect the results. The actual calculation is activity per unit weight times weight collected, divided by area sampled. The pertinent question relates to the representativeness of the grams of sample to the sampled area. Minor variations in the sampled depth probably have more affect on the interpretation of the results than on the actual numerical values.

Terzaghi and Peck (1968) present information on compressibility and the hysteresis loop after removal of the compression force for soil. A force of about 10-20 pounds applied to a scoop with frontal area of 50 cm^2 (10 cm x 5 cm) may produce a change in the void ratio (e) of up to about 10 percent of its value. The void ratio is the ratio of the volume of voids to the volume of soil substance. By relating the change in e to the change in porosity, n, ($n = e/1+e$), the change in the field bulk density of the soil can be estimated.

If the cutting edges of the scoop are assumed to transmit the force as a compression force to the total frontal area of the scoop, the bulk density at the frontal interface of the scoop is increased by roughly 5 percent. But part of the compressed soil would be in the scoop, and the compression would be reduced with distance from the scoop frontal interface. Thus, the maximum reasonable error would be less than 5 percent. This error would appear as a reduction in the actual amount of soil taken as a sample.

The bulking of the soil, as it is disturbed by inserting the scoop, tends to make it mound up in the scoop. Unless this is recognized, the tendency would be to only take a deep enough sample to fill the scoop, thus underestimating the volume sampled by about 20 percent. Bulking can also cause losses of material while taking the sample to be overlooked. Data from Terzaghi and Peck (1968) indicate potential errors of up to about 20 percent.

The EMSL-LV program has incorporated the use of scoops having an extra 2 cm length (10 cm sampling length, plus 2 cm for bulking, etc.) to minimize bulking and compression errors.

Taking profile cuts adjacent to each other could result in errors of roughly 10 percent, due to the disturbed nature of the soil and thus reduced bulk density, even if extreme care is taken in positioning the scoop on the open face of the second cut.

All of these errors tend to minimize the amount of sample actually obtained from an assumed area sample. This is apparently illustrated by the histograms of apparent soil density for the Trinity results as shown in Figure 2.

An experiment was conducted by EPA - Las Vegas staff to obtain an indication of variations in the soil volume collected by the scoop technique for depth profiles. Samples were taken by three experienced teams from a 10-meter diameter circle of relatively undisturbed desert. Two of the teams (A and B) basically used the NAEG scoop profile technique. The third team (C) used a displacement technique where the volume of soil removed was measured by filling the hole with a known volume of a standard density sand.

Team A actually took two side-by-side scoops (10 x 10 x 5 cm deep) from a trench. Not only were the scoops taken side by side, but a bench was not cleared off before going to the next lower depth. Team B took a single scoop. A bench was not cleaned off before sampling at the next depth.

Each team took four profiles. The only significant error noted was the sampling depth. Team A sampled to a depth of 22.9 cm versus the design depth of 20 cm.

Team B sampled to depths of 21.6 to 22.23 cm. These depth errors are equivalent to bulk density errors of about 10 percent. However, assuming the errors were generally uniform and that the actual sampling depths were measured, the bulk densities can be corrected.

The average bulk densities (wet weight) for the four profiles for teams A and B were 1.70 and 1.62 g/cm^3. Correcting for the sampling depth gives values of 1.49 and 1.48 respectively. These values compare well to the value of 1.53 g/cm^3 for team C. The standard deviation for all three sets of data was about 0.05 g/cm^3, indicating overlap of the data.

An interesting speculation is that concern for bulking of the sample and fear of not taking an adequate depth appears to result in over-compensation. The sampling depth may be deeper than expected.

Significance of Sampling Depth

The sample depth increment has a significant impact on sample results, and is inherently related to the objectives of the sampling program. This is just as true for results reported as activity per unit soil mass as for those reported as activity per unit area. Plutonium is deposited on the surface of the soil. Through mechanical action, as well as water and earthworm movement, etc., it is mixed through the upper soil layers, down to 20 cm, or more. The relative concentration with depth varies

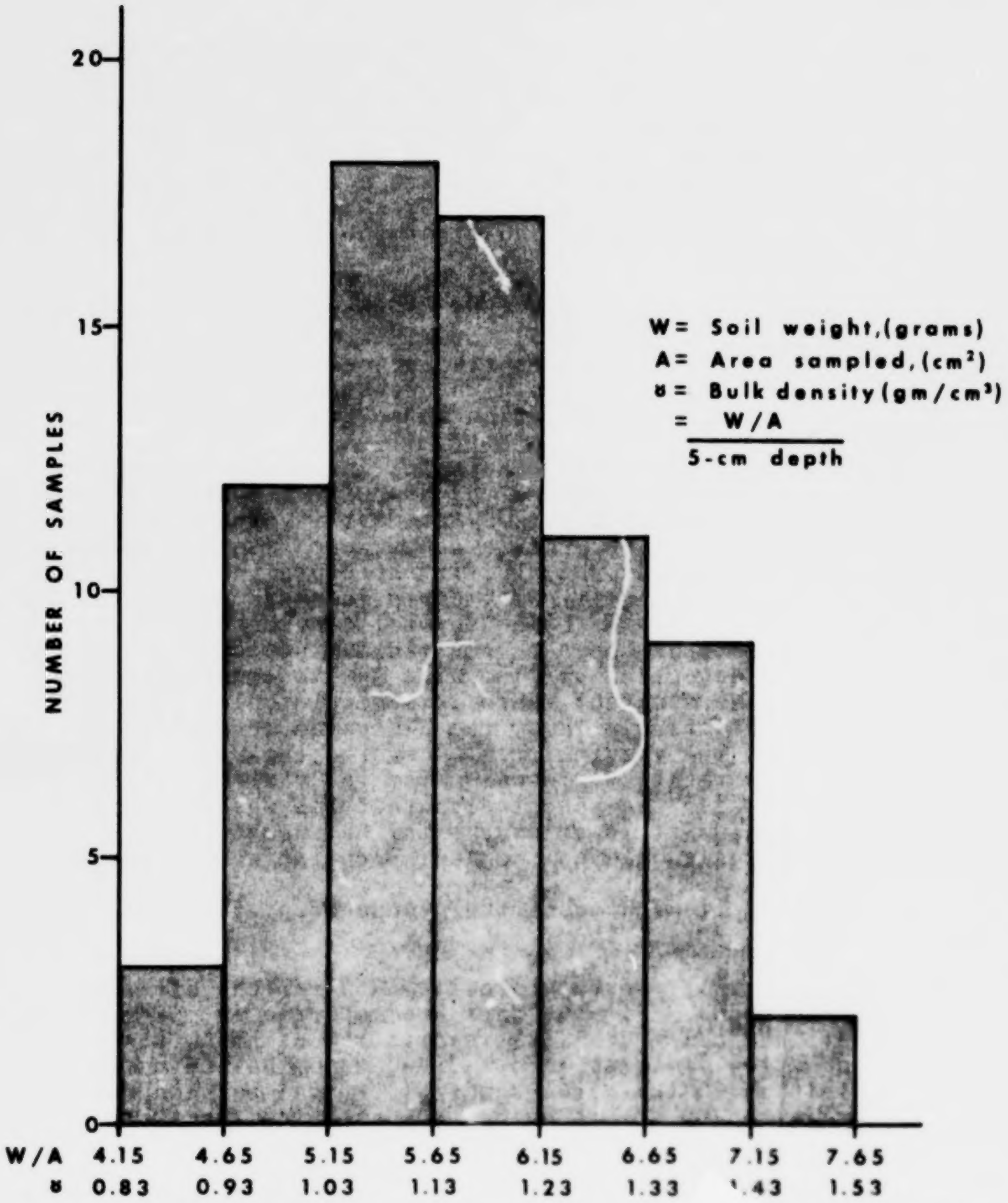

Figure 2. Histogram of weight per unit area of 72 soil samples from vicinity of Trinity, New Mexico. (from Douglas, EPA/ORP-LVF, unpublished data)

within localities and from one geographical area to another. Leopold et al. (1966), Colby (1963), EPA (1973a), Chepil (1945a, b,c,d), Chepil (1946), and Chepil and Woodruff (1963) present information on soil denuding, transport, and erosion as a result of natural forces and of human land-use.

Data on plutonium soil profiles from numerous areas are summarized in Table 5. These data include results from Savannah River, Georgia; NTS, Nevada; Rocky Flats, Colorado; New York, New York; and Trinity, New Mexico. The range of results, means, and standard deviations are given for the various sites. This presentation inherently assumes the data are normally distributed. This hypothesis has not been tested. Given the range and scatter of the data, the summarization and treatment is presented only as a trend or indication.

It is readily apparent that some of the groups of data, such as those reported by Bliss (1973) for NTS are not normally distributed. The data are inherently bounded by a value of 100 percent, and a value of the mean plus one standard deviation exceeds the 100 percent accumulation in several instances.

It is difficult to obtain meaningful information from some of the data because they are reported as pCi/g with no indication of the bulk density of the soil. Since most investigations vary the vertical increment with profile depth, each sample represents an average of a composite over a different depth increment. The variation of soil bulk density with depth further complicates the comparison. Also, at depths below several centimeters, the plutonium concentrations approach the minimum detectable activity (MDA)*. Given the detection of plutonium at the lower depths in many profiles, it is apparent there is some plutonium down to about 20 cm in most cases. Thus, the plutonium concentration postulated for the MDA results (e.g., zero to the MDA) influences estimates of the percent of plutonium for the various soil strata. There is also the speculation that the observed concentrations of plutonium at lower depths may be due to cross-contamination during sample collection, preparation, or analysis.

The following items discuss the groups of profile data in Table 5.

1. Bliss (1973) presents profile data for the off-site area around NTS. The data are reported in pCi/g of dry soil and nCi/m^2. Bliss reports values below the detection limit as zero. Given a nominal detection limit of 20 fCi/g (0.02 pCi/g), it can be seen that the exclusion of values below the detection limit can have a significant impact on the cumulative percent deposition for locations having deposition near background--roughly 1 nCi/m^2. For example, for the Furnace Creek-1 sample, the only detectable result in the profile was

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*MDA (minimum detectable activity)

TABLE 5. PERCENTAGE PLUTONIUM DISTRIBUTION IN SOIL AS A FUNCTION OF DEPTH

Location	Reference	0-1 cm Depth				0-2.5 cm Depth				0-3 cm Depth				0-5 cm Depth				0-15 cm Depth			
		n*	$\bar{x}$*	S*	Range	n	$\bar{x}$	S	Range	n	$\bar{x}$	S	Range	n	$\bar{x}$	S	Range	n	$\bar{x}$	S	Range
Nevada Test Site, NV^{2}	Bliss (1973)	39	52	32	0-100%	-------				41	91	20	16-100%	-------				41	99	5	76-100%
Nevada Test Site, NV^{3}	Gilbert & Eberhardt (1974)	-------				-------				-------				13	97	3	90- 99%	-------			
Rocky Flats, CO	Krey & Hardy (1970)	-------				-------				-------				7	62	17	39- 91%	-------			
Rocky Flats, CO^{1}	Poet & Martell (1972)	7	52	38	3- 94%	7	69	33	17=100%	-------				5	83	27	39-~100%	-------			
Trinity Site, NM	Douglas	-------				-------				-------				4	50	24	27- 84%	4	79	22	46- 95%
New York City, NY	Krey & Hardy (1970)	-------				1	66	--	--	-------				1	81	--	--	-------			
Waynesville, OH	Krey & Hardy (1970)	-------				-------				-------				1	47	--	--	-------			
North Eastham, MA	AEC (1974$_a$) Wash-1359	-------				1	~53	--	--	1	~69	(@ 4 cm)		1	~77	(@ 6 cm)		1	~90	--	--
Savannah River, GA^{2}	AEC (1973$_a$) Wash-1259	-------				-------				-------				7	61	7	48- 73%	7^{2}	91	4	--

1. Depth intervals are missing from several profiles. The interval was 0-1.3 cm versus 0-1 cm. Deposition was calculated from the original data by assuming a bulk density.
2. Most of the profiles indicated undetectable plutonium levels below 15 cm.
3. Excludes two values of 38 and 46.6%. These values give $\bar{x}$ = 90; S = 20.

*n = number of samples

*$\bar{x}$ = mean Pu in increment, as percent of total deposition.

*S = standard deviation

0.02 pCi/g. This then indicates 100 percent of the activity was in the first centimeter of soil.

If it is postulated that all the samples contain 0.01 pCi/g (about one-half the nominal MDA), the following profile is noted:

Depth (cm)	Bliss (pCi/g)	Postulated pCi/g	Calculated nCi/m *	Postulated Cum %	Bliss Cum %
0-1	0.02	0.02	0.3	9	100
1-3	0	0.01	0.2	15	-
3-7	0	0.01	0.5	29	-
7-15	0	0.01	1.2	65	-
15-23	0	0.01	1.2	100	-

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* Calculated by assuming soil density of 1 g/cm^3 from 0-5 cm and 1.5 g/cm^3 from 5-23 cm.

The postulated values differ from Bliss' estimates, for this extreme example, by over a factor of 10. If a level equal to the MDA were postulated, the difference would be a factor of 20. The assumption of zero for MDA values can easily account for variances of tens of percent in the cumulative deposition. With a lower MDA, this effect would decrease.

The following items summarize specifics from Bliss (1973):

1. A large fraction of the total plutonium is generally in the top centimeter of soil.
2. The top 5 cm of soil generally contains over 90 percent of the detected activity.
3. Excluding one sample (Moapa-1), whose values are at or near the MDA, 50 percent or more of the detected activity is in the top 3 cm of soil.

Gilbert and Eberhardt (1974) summarize profile data from Areas 5 and 13 on the NTS. The following observations can be drawn from their data:

1. Thirteen of 15 profiles indicated over 90 percent of the detected plutonium was in the top 5 cm for desert

TABLE 5. PERCENTAGE PLUTONIUM DISTRIBUTION IN SOIL AS A FUNCTION OF DEPTH

Location	Reference	0-1 cm Depth				0-2.5 cm Depth				0-3 cm Depth				0-5 cm Depth				0-15 cm Depth			
		n*	$\bar{x}$*	S*	Range	n	$\bar{x}$	S	Range	n	$\bar{x}$	S	Range	n	$\bar{x}$	S	Range	n	$\bar{x}$	S	Range
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Waynesville, OH	Krey & Hardy (1970)	-------				-------				-------				1	47	--	--	-------			
North Eastham, MA	AEC (1974a) Wash-1359	-------				1	~53	--	--	1	~69	(@ 4 cm)		1	~77	(@ 6 cm)		1	~90	--	--
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1. Depth intervals are missing from several profiles. The interval was 0-1.3 cm versus 0-1 cm. Deposition was calculated from the original data by assuming a bulk density.
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3-7	0	0.01	0.5	29	-
7-15	0	0.01	1.2	65	-
15-23	0	0.01	1.2	100	-

* Calculated by assuming soil density of 1 g/cm^3 from 0-5 cm and 1.5 g/cm^3 from 5-23 cm.

The postulated values differ from Bliss' estimates, for this extreme example, by over a factor of 10. If a level equal to the MDA were postulated, the difference would be a factor of 20. The assumption of zero for MDA values can easily account for variances of tens of percent in the cumulative deposition. With a lower MDA, this effect would decrease.

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Gilbert and Eberhardt (1974) summarize profile data from Areas 5 and 13 on the NTS. The following observations can be drawn from their data:

1. Thirteen of 15 profiles indicated over 90 percent of the detected plutonium was in the top 5 cm for desert

pavement areas. The other two areas gave values of 38 and 47 percent.

2. The average of the 13 values is given in Table 5. The mean for all the values is 90 percent with a standard deviation of 20 percent.

3. The averages for Areas 13 and 5 are similar. However, if the two low values are included, the mean for Area 13 is lower than that for Area 5. The two low values also cause a large increase in the standard deviation.

4. The authors conclude that most of the profiles have greater than 95 percent of the plutonium in the top 5 cm. The actual data are not presented, so the presence and treatment of MDA values cannot be assessed.

5. The authors noted a trend toward a decrease in the plutonium:americium ratio with depth.

Krey and Hardy (1970) present profile data for Rocky Flats, New York City, and Waynesville, Ohio. The following points are noted:

1. Only about 62 percent of the plutonium was found in the top 5 cm.

2. As much as 60 percent was found below 5 cm.

Poet and Martell (1972) report data for the Rocky Flats area. Their profiles generally extended to only 10 cm or less; and several increments are missing in the reported data. Furthermore, the data were only reported in units of dpm/g. The data were transformed to units of nCi/m^2 by multiplying by the incremental depth of the sample and a postulated bulk density. The density from 0-5 cm was assumed to be 1 g/cm^3 (based on Poet and Martell, 1972, and random estimates derived from Krey and Harty, 1970). A density of 1.5 g/cm^3 was used for samples below 5 cm (estimated from Krey and Hardy, 1970).

Table 6 (data from Poet and Martell, 1972) indicates general uncertainties in the data as a result of the sampling techniques for the profiles (fractions of a centimeter to a centimeter), the previously mentioned transformation assumptions, point-to-point variations, etc.

TABLE 6. COMPARISON OF SURFACE AND PROFILE SAMPLES

Location	Profile Depth (cm)	Estimated cumulative deposition based on depth profile (nCi/m²)	Estimated deposition based on 1 cm-deep surface sample* (nCi/m²)
J	0-0.3	6.27	
	0-1.3	14.06	5.18
K	0-0.3	6.78	
	0-1.3	4.01	3.97
I	0-0.3	0.12	
	0-0.7	0.21	7.75 (Taken prior to profile)
	0-0.7 plus 1.3-2.5	0.45	

* Different data from profile sample

The variations between surface samples and profile samples from similar depths range from over two to greater than an order of magnitude. Poet and Martell (1972) note a large build-up of soil from wind erosion at Site I subsequent to taking these samples, which probably explains the apparent discrepancy for that site. However, it should be emphasized that this was not noted when the samples were first taken. This indicates the problems in taking characteristic samples--hindsight helps.

The following items characterize the Poet and Martell data:

1. About 52 percent of the detected plutonium was found in the first 1.3 cm of soil.
2. About 69 percent was found in the top 2.5 cm of soil.
3. About 83 percent was found in the top 5 cm of material. Given the calculated standard deviations, the range and limitations of the data, and the assumptions necessary to transform the data, the value of 83 ± 23% for Poet and Martell is considered similar (not statistically different even at low probabilities) to the value of 62± 17% for Krey and Hardy.

Data for the Trinity, New Mexico site are based on four samples taken in November 1973. The data will be published in a future ORP-LVF report. The concentrations ranged up to 1 pCi/g and 47 nCi/m^2.

Since actual MDA values were reported, the concentration was postulated to be equal to the MDA. The percentage of total deposition for 0-15 cm becomes 78 percent with an S of 16 percent. These values are essentially indistinguishable statistically.

Data from the Savannah River plant were transformed from pCi/g to nCi/m^2 as indicated previously. All but one of the profiles indicated values below the MDA for strata below 15 cm. Thus, the first value below the detectable limit was set equal to the MDA.

The profile from North Eastham, Mass. (AEC, 1974b) is from a background location.

The most general conclusion that can be drawn from the summary of profile data in Table 5 is that the initial phase of a soil sampling program should include profile samples to characterize the area. Further, 5 cm is a prudent minimum depth for surface samples.

A non-weighted average of the values in Table 5 indicates that 72% ± 18% (1 sigma) of the activity is above 5 cm. Given the potential for bias in the various groups of data, a non-weighted mean appears to be reasonable. If the values in the table are weighted by the number of results represented by each value, the average is 83 percent.

Table 7, taken in part from Krey (1974) compares some of his data with that from Poet and Martell (1972). Krey notes that Poet and Martell's data are generally low by a factor of 10. This evaluation is based on Poet and Martell's data for the top 1 cm of soil, and Krey's data for a 20 cm sampling depth.

It should be noted that these data are very difficult to compare due to the difference in sampling depth, and possibly more importantly, Poet and Martell only report their data in pCi/g. If a surface soil density of 1 g/cm^3 (suggested by Poet and Martell, and used by Krey for the comparison) is used for the first 5 cm, and 1.5 g/cm^3 for the 5 to 15 cm increment, some of the Poet and Martell data can be related to the same general depth used by Krey (1974). Three values are presented in Table 7.

Poet and Martell (1972 and 1974) note that their objective was to detect the recent deposition of plutonium and indicate an inhalation hazard - thus their choice of a shallow sampling depth. In any case, although the original data in Table 7 indicate a significant disagreement between the two sets of data, the data for similar sample depths are generally compatible.

TABLE 7. COMPARISON OF PLUTONIUM SOIL SAMPLING DATA

Site	Poet and Martell Data			Krey & Hardy Estimate
	(nCi/m^2) 1 cm surface sample	(nCi/m^2) profile data	Profile depth (cm)	(nCi/m^2)
A	5.8			15
B	10			35
	61			35
C	0.41			11
	0.26			11
I	7.7	3	14	4
J	5.4	15	10	20
K	4.0	11	2.5	14
L	0.52			17
M	1.7			17
N	6.0			30
V	1.4			4
V	2.4			8
W	0.15			17
Z	0.84			4

It appears, based on the comparisons in Table 7 of the Poet and Martell and the Krey data, and the similar tabulation in Table 6, that a 1-cm sample depth results in a large variation of the data. This is reflected by the large standard deviation noted in Table 5.

Discrete Particulate Material

Various authors (Poet and Martell, 1972, and Sill, 1971) have related variations between samples to discrete particles, whereas other authors relate variations to inadequate sample collection and aliquoting techniques (Krey and Hardy, 1970 and 1974). Sill (1971) and Sill and Hindman (1974) emphasize the limitation of various analytical techniques for complete dissolution of refractory plutonium particles. They not only indicate concern with insoluble refractory material in the original sample, but also with the formation of refractory material during sample preparation. This section is only concerned with the sampling implications of discrete particles. The analytical implications will be dealt with in another section.

Plutonium contamination in the environment does not appear to be in the form of discrete particles composed of plutonium oxides. Rather, soil and air particles containing plutonium appear to be composed of natural particles with plutonium oxides generally dispersed in the particle or natural particles agglomerated with one or more plutonium oxide particles (Nathans and Holland, 1971, and Bretthauer et al., 1974). The actual characteristics of the particles is expected to vary depending on the source of formation and release (e.g., plutonium in oil leaking from drum at Rocky Flats, and explosive detonations at NTS).

Table 8 indicates characteristics for various size particles.

TABLE 8. PLUTONIUM PARTICLE CHARACTERISTICS

Isotope	Diameter (μm)	pCi per particle	particle per pCi	Particle per gram of soil for 0.1 pCi/g	Particle per 930 cm^2 @ 1 nCi/m^2
^{239}Pu	0.1	0.000325	3076	308	286,000
	1	0.325	3.077	0.308	286
	1.5	1.096	0.912	0.091	84.8
	2	2.60	0.385	0.039	35.8
	5	40.59	0.0246	0.0025	2.29
^{238}Pu	0.1	0.09	11.1	1.1	1021
	1	90.99	0.0110	0.0011	10.2
	1.5	307	0.0033	0.00033	0.30
	2	728	0.0014	0.00014	0.13
	5	11,370	8.8E-5	8.8E-6	0.008

Ettinger et al. (1967), Mishima and Schwendiman (1970), Kelkar and Joshi (1970), Molen and White (1967), Sherwood and Stevens (1965), Hunt (1971), Mishima (1964), and Kirchner (1966) present data on particle size distributions expected and observed around various types of plutonium operations and accidents. The mean sizes vary from less than one to tens of micrometers (Mishima, 1964, and Mishima and Schwendiman, 1970). The most probable geometric mean sizes for release appear to be around 1 micrometer, with geometric standard deviations of about 1.5 to 3. Nuclear explosions apparently produce particles a few millimicrometers in diameter (Klement, 1965).

Although the agglomeration of plutonium particles to soil and dust particles changes the basic size distribution, the activity per aggregate particle should relate to the original plutonium particle or particles. Thus, for samples near facilities associated with plutonium releases, it is possible that the contamination is composed of two or more particle size distributions (worldwide fallout and facility) with one of the distributions in the micrometer size range. Thus, as noted by Sill (1971), the deposition near such facilities may be heterogeneous, when viewed from one-, 10-, or even 100-g samples. Table 8 shows the number of particles in a sample of given size.

If samples are based on a significant fraction of a 1000 cm^2 area (929 cm^2 per ft^2) the homogeneity of plutonium deposition within the area is less critical than is the homogeneity within the sample aliquot taken for actual analysis.

Table 9 presents a set of results from Sill (1971). Geometric means, $\bar{X}$, and geometric standard deviations, S, have been calculated for the various groups of data. The column on the right indicates the ratios of the maximum to minimum values for the 95 percent confidence range. The first two samples were collected from an area that should have only been exposed to global fallout. The values for the duplicate analyses reflect expected analytical variations (Sill, 1971). It should be noted that the background concentrations varied by a factor of two. This could possibly relate to different sample depths, in which case the deposition numbers (nCi/m^2) might have less variance.

The third through seventh samples (Table 9) were collected downwind of a facility where there was a known release. This is evident in the observed plutonium concentrations and general increase in the ratio of the 95 percent confidence limits, which indicates more heterogeneous distribution. Sample 7, which was 43 miles downwind, is an exception to both the concentration and heterogeneous distribution comments. Sample 4, although elevated, also indicates a fairly uniform distribution. Samples 8 and 9 are from another facility with a known release. The larger range for Sample 8 is due to only one result. The general scatter in the duplicate results for Sample 9 and the range in the 95 percent limits reflect that it was collected near the facility, apparently in an area of heterogeneous deposition.

Many of the variations in Table 9 can be accounted for by micrometer-size particles of PuO_2. The activity of plutonium particles is proportional to the diameter cubed of the particle. Thus, using data from Table 8, the high result for Sample 3 (Table 9) could have been due to about one 1-micrometer particle

TABLE 9. REPRODUCIBILITY OF ANALYSES USING 10-GRAM ALIQUOTS OF PREPARED SOILS

(From Sill, 1971)

Number	Measured Pu-239 (dpm/g)	Location or Type Sample	ln $\overline{x}^a$	ln S	t (95%)	$\overline{x}$	Ratio of Upper and Lower 95% Confidence Limits
1	0.110 ± 0.009 0.116 ± 0.010 0.112 ± 0.012 0.101 ± 0.008 0.111 ± 0.008	General Bkgd.	-2.21	0.051	2.776	0.11	1.3
2	0.060 ± 0.007 0.050 ± 0.007 0.054 ± 0.008 0.063 ± 0.007	General Bkgd.	-2.87	0.104	3.182	0.056	1.9
3	1.59 ± 0.04 0.56 ± 0.02 0.94 ± 0.03 0.68 ± 0.03	2 miles downwind of facility with Pu release.	-0.141	0.456	3.182	0.87	18
4	0.62 ± 0.02 0.56 ± 0.02 0.57 ± 0.02	2 miles downwind of facility with Pu release.	-0.540	0.054	4.303	0.58	1.6
5	0.044 ± 0.006 0.077 ± 0.008 0.042 ± 0.005 0.055 ± 0.010 0.047 ± 0.006	16 miles downwind of facility with Pu release.	-2.96	0.245	2.776	0.052	3.9

TABLE 9. REPRODUCIBILITY OF ANALYSES USING 10-GRAM ALIQUOTS OF PREPARED SOILS (From Sill, 1971) (Continued)

Number	Measured Pu-239 (dpm/g)	Location or Type Sample	ln $\overline{x}$[a]	ln S	t (95%)	$\overline{x}$	Ratio of Upper and Lower 95% Confidence Limits
6	0.079 ± 0.009 0.058 ± 0.008 0.071 ± 0.009 0.29 ± 0.01	17 miles downwind of facility with Pu release.	-2.32	0.731	3.182	0.099	104
7	0.051 ± 0.007 0.066 ± 0.009 0.056 ± 0.006 0.052 ± 0.006	43 miles downwind of facility with Pu release.	-2.88	0.117	3.182	0.056	2.1
8	0.071 ± 0.008 0.22 ± 0.02 0.051 ± 0.007 0.059 ± 0.006	50 miles downwind of facility with Pu release.	-2.49	0.665	3.182	0.083	69
9	0.35 ± 0.02 0.78 ± 0.04 1.73 ± 0.04 0.26 ± 0.01	100 yds. downwind of facility with Pu release.	-0.524	0.852	3.182	0.592	227

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[a] The analytical error estimates have not been considered in the statistical summarization of the data.

per gram, or a single particle having a diameter of about 2.5 micrometers in the total 10-gram sample, above the global background.

As part of the NAEG program, a set of 20 soil samples were collected from Penoyer Valley, Nevada, about 20 miles northeast of the NTS. The samples were split into duplicates and two aliquots were taken from each duplicate. The scatter of results from these 80 samples was such that the variations between the four positions from an individual site and the 80 samples could not be related to a rational explanation of sampling or analytical errors.

In an attempt to resolve this problem, portions of the sample from one site were split for inter-laboratory analyses. Table 10 shows replicate aliquot analyses of the sample by three laboratories. Each laboratory used its standard analytical method to analyze aliquots of less than 10-mesh desert soil. Most of these data were published by Bliss (1973). Although the sample preparation and analysis techniques vary somewhat between the three labs, they are basically the same. The analyses were all done by the basic acid dissolution technique (HCL, HF, and HNO). The specific techniques vary, in part, because of the different sample sizes.

Although the geometric means from the different labs vary, all of the 95 percent confidence levels (C.L.) have a significant overlap. These data illustrate the dramatic decrease in the ratio of the extremes of the 95 percent confidence range with the increase in sample size.

The geometric mean and standard deviation for the 80 replicate results, and the 95 percent C.L. estimates and their ratios are given in Table 11. The mean and C.L. estimates and their ratios include the values from Table 10. This would be expected, since the group of 80 replicates is based on a sample from four sites, whereas the interlaboratory samples came from one of the four sites. A frequency distribution table and probability plot for the 80 values is shown in Appendix C.

Means, confidence levels, and ratios of the C.L. are given for three other groups of data in Table 11 (Bliss, 1973). The samples from Baker, California and Kingman, Arizona and northwest of NTS indicate background values and have much lower C.L. ratios than the other two samples. The Baker and Kingman group of data represents several sites, and thus would be expected to have a larger range than the data from the location northwest of NTS.

TABLE 10. COMPARATIVE ANALYSES OF PLUTONIUM-239 IN SOIL

Lab	Aliquot Size (g)	Pu-239 (pCi/gm)	ln $\overline{x}$	ln S	$\overline{x}$	Range 95% C.L.	Ratio of Upper and Lower 95% Confidence Limits
EPA	1	0.23	0.405	0.952	0.67	0.085-5.21	61
	1	0.24					
	1	0.27		(n = 14; t = 2.16)			
	1	0.37					
	1	0.30					
	1	0.40					
	1	0.42					
	1	0.53					
	1	0.67					
	1	1.0					
	1	1.2					
	1	1.4					
	1	3.0					
	1	5.3					
REECo	10	0.66	0.646	0.674	1.9	0.415-8.76	21
	10	0.90					
	10	1.3		(n = 10; t = 2.26)			
	10	1.4					
	10	1.5					
	10	2.0					
	10	2.6					
	10	3.3					
	10	4.4					
	10	5.2					

TABLE 10. COMPARATIVE ANALYSIS OF PLUTONIUM-239 IN SOIL
(Continued)

Lab	Aliquot Size (g)	Pu-239 (pCi/gm)	ln $\overline{x}$	ln S	$\overline{x}$	Range 95% C.L.	Ratio of Upper and Lower 95% Confidence Limits
LLL	25	1.9	1.078	0.6312	2.9	0.97-10.32	11
	25	4.6					
	25[a]	3.3	1.226	0.0415	3.4		
	25[a]	3.5					
	100	4.1	1.565	0.213	4.8	2.33-10.4	4.5
	100	5.5					
	100[a]	4.0	1.635	0.3374	5.1		
	100[a]	6.5					

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[a] Aliquot received additional grinding and blending prior to analysis.

TABLE 11. PERTINENT STATISTICS FOR Pu-239 RESULTS FROM SELECTED SAMPLE GROUPS (from Bliss, 1973)

	Location and Units of Activity			
	Baker, CA and Kingman, AZ (nCi/m^2)	Penoyer Valley Replicate Site (pCi/g)	Northeast of NTS (nCi/m^2)	Northwest of NTS (nCi/m^2)
No. of Results	27	80	100	35
ln X	0.068	0.053	1.881	0.584
ln S	0.869	1.336	1.261	0.572
X	1.071	1.054	6.557	1.793
Lower 95% C.L.	0.188	0.0729	0.527	0.571
Upper 95% C.L.	6.086	15.245	81.638	5.627
Ratio:				
Upper to Lower C.L.	32	209	155	10

The sample from northeast of NTS is at the extreme of or above background. The Penoyer Valley results are generally indicative of roughly 10 nCi/m^2 or higher. Thus, both of these samples appear to contain dispersed global fallout, plus rather discrete NTS fallout.

The variation in the analyses of these samples is relatable to a variance of one or several particles, of one to several micrometer diameter, per gram of sample. The actual numbers depend on the particle size and sample size of concern. The potential variation in results for 1-gram samples is particularly obvious. A single one-micrometer particle can cause a multiple variance in results. This would give strong credence for taking a minimum sample aliquot of 10 grams for analysis.

Little et al. (1973) present a limited amount of data for soil grain size in the Rocky Flats areas and the percent of plutonium associated with the various grain size increments. The plutonium concentration, pCi/g, for two samples is inversely proportional to the soil grain size, 0.1 to 5 mm. Tamura (1975) presents similar data (see the end of this section).

The heterogeneous deposition of plutonium-238 presents an even greater problem than for plutonium-239, because the specific activity of plutonium-238 is about 280 times that of plutonium-239. Furthermore, the concentration of plutonium-238 in the environment is normally much lower than that of plutonium-239. Plutonium-238 background levels are roughly 1 fCi/g for soil samples several cm deep (Krey and Hardy, 1970, and Robinson et al., 1975). Thus, from Table 8 it can be seen that a plutonium-238 dioxide particle of one micrometer diameter in a 10-gram sample can give a value of 9 pCi/g, or four orders of magnitude above background. Even a 0.1-micrometer particle in a 10-gram sample gives a value of 9 fCi/g.

Robinson et al. (1975) report results of two programs where samples were split between Mound Laboratory and EPA. The ratios of the results of these programs are shown in Table 12. The samples collected by EPA were split in the field. The samples taken by Mound Laboratory were first dried and ground to less than 20-mesh particle size. It is evident from Table 12 that the samples split after mixing gave more comparable results than did those which were split in the field.

TABLE 12. INTERLABORATORY COMPARISON OF MOUND LABORATORY AND EPA RESULTS OF PLUTONIUM-238 IN SOIL AND SEDIMENT
(From Robinson et al., 1975)

Samples Split in Lab

Code	Mound (nCi/g)	EPA (nCi/g)	Ratio of Results Mound/EPA
EA1	0.0001 ± 0.0001[a]	0.00011[b]	0.91
EB1	<0.0001[a]	0.00012[b]	< 0.83
EC1	0.0029 0.0011	0.0048	0.60
ED1	0.0009 ± 0.0004	0.0011	0.82
EE1	0.425 ± 0.024[a]	0.440	0.97
EF1	1.03 ± 0.05[c]	1.13[b]	0.91
EG1	0.0098 ± 0.0027	0.0108	0.91
EH1	0.0238 ± 0.0053	0.026	0.92
EI1	<0.0001	0.00098	< 1.02
EJ1	0.0010 ± 0.0005	0.0011[b]	0.91
FA1	0.0094 ± 0.0026	0.0085[c]	1.11
FE1	0.0138 ± 0.0025[b]	0.0181	0.76
GA1	0.0004 ± 0.0002	0.00048	0.83
HA1	0.0047 ± 0.0016	0.0051	0.92
IA1	0.0020 ± 0.0008	0.0025	0.80
JA1	0.0007 ± 0.0004	0.0007	1.00
KA1	0.0309 ± 0.0065	0.027	1.14
LA1	0.0096 ± 0.0027	0.0109	0.88
CE1	0.0302 ± 0.0064	0.024	1.26
QE1	1.00 ± 0.09	0.920	1.09

n=20
$\bar{X}$=0.929
S=0.147

[a] Mean of quadruplicates
[b] Mean of duplicates
[c] Mean of triplicates

TABLE 12. INTERLABORATORY COMPARISON OF MOUND LABORATORY AND EPA RESULTS OF PLUTONIUM-238 IN SOIL AND SEDIMENT
(From Robinson et al., 1975)
(Continued)

Samples Split in Field

Code	Mound (nCi/g)	EPA (nCi/g)	Ratio of Results Mound/EPA
EPA-17	0.284 ± 0.035	0.047	6.04
EPA-18	0.280 ± 0.035	0.060	4.67
EPA-1	0.165 ± 0.023	0.230	0.72
EPA-6	0.0052 ± 0.0017	0.0038	1.37
EPA-20	0.0011 ± 0.0005	0.0019	0.58
EPA-14	0.0009 ± 0.0004	0.00044	2.05
EPA-15	0.0009 ± 0.0004	0.00096	0.94
EPA-3	<0.0001 ± 0.0001	0.00039	<0.26
EPA-13	<0.0001 ± 0.0001	0.00010	<1.00
EPA-7	<0.0001	0.00044	<0.23
EPA-12	<0.0001	0.00019	<0.53
EPA-2	<0.0001	0.00012	<0.83
			n=12 $\bar{x}=1.60$ S=1.84
ALGAE SAMPLES			
EPA-9	0.111	0.079	1.41
EPA-21	0.0024	0.00088	2.73
			n=2 $\bar{x}=2.07$ S=0.93

PARTICLE SIZE DISTRIBUTION OF PLUTONIUM IN SOIL

Although inhalation is generally considered to be the primary intake pathway for plutonium, soil is generally considered to be the primary reservoir of environmental contamination. Thus, there is a need to relate soil sample results to potential or actual airborne concentrations. The first part of this section has addressed techniques primarily intended to quantitate the amount of plutonium in soil. Thus, the emphasis has been to take samples of a reproducible and sufficient depth in order to assess the total plutonium inventory. Sampling for resuspendible plutonium requires different priorities and considerations. Presently applied techniques include a one-eighth inch depth sample by the State of Colorado, 1-cm depth samples by Poet and Martell (1972), and techniques using sticky paper placed in contact with the soil surface (Volchok, 1971).

More recently, McLendon et al. (1975) published results where a vacuum cleaner type instrument was used to collect the resuspendible material from the area of the sample head. This technique appears to have merit, but sample results have not been directly related to air concentrations.

Johnson et al. (in press) proposed that the less than 5-micrometer (density 11 g/cm^3; i.e., 17 micrometer density 1 g/cm^3)*size material that can be swept from the soil surface be used as an indication of inhalation hazard. The sample fractionation procedure includes breaking the soil down to basic discrete particles. Thus, the technique would appear to reverse the "weathering" effect that decreases the relative resuspendibility of old versus newly deposited contamination (Anspaugh et al., 1975).

There presently is no accepted technique for measuring resuspendible material from soil. However, data from several studies allude to soil being associated with various particle size fractions (Johnson et al., Little et al., 1973, and Tamura, 1975). Since resuspension is dependent on the soil particle size distribution (Anspaugh et al. 1975), as well as other factors, the size distribution of plutonium in soil is considered to be pertinent basic information.

The ORP-LVF obtained several samples from Rocky Flats to independently investigate the size distribution of plutonium in the soil. The samples were collected by the Rocky Flats Environmental Research and Development Administration area office several hundred yards downwind of the pad where the basic Rocky Flats plutonium contamination incident originated. Although it was originally presumed that the samples would contain less than about 25 pCi/g of plutonium-239, they actually contained over 500 pCi/g. Thus, because of concern for laboratory contamination, they received less extensive analysis than originally proposed.

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*The use of a density of 1 g/cm^3 is based on the definition of the equivalent aerodynamic diameter. Conversions to equivalent diameters in this section are based on the settling velocity in air--see next section.

A sample from about 35 miles downwind at the Trinity, New Mexico site was also analyzed.

The Rocky Flats samples were collected in February 1976 from the surface centimeter of soil, from an area of 2000 cm^2. The Trinity sample was collected in December 1974. It represented the surface 2.5 cm of soil from an area of 2500 cm^2.

Two Rocky Flats samples were partitioned into three separate aliquots. The aliquots were further partitioned as described below (the aliquots are denoted as A, B, and C in Table 13).

1. Dry sieve through 10-mesh sieve--Less than 2 mm

2. Wet sieve (not dried material) through 140-mesh sieve--Less than 102 micrometer

3. Elute material from sedimentation column for a Stoke's Law setting velocity of less than 3.37×10^{-3} cm/sec--(10 micrometer at 1 g/cm^3, or 6.1 micrometer at 2.65 g/cm^3; Krumbein and Pettijohn, 1938)

The samples were prepared according to the general techniques presented by Folk (1961). The following comments relate to specific information on the sample preparation procedure:

1. Radiochemistry was performed on about 10-gram aliquots of the samples.

2. The samples were not completely dried prior to sieving (forms and increases the stability of conglomerates, Falk, 1961).

3. A solution of Calgon, sodium metaphosphate, was used as a dispersing agent for the sedimentation separation (about 10 ml of a solution of 40 g/liter).

4. The material retained on the 10-mesh sieve was washed with a solution of Calgon, and the wash included with the less than 10-mesh material.

5. The material retained on the 140-mesh sieve during wet sieving was then dry-sieved through the 140-mesh sieve. Folk (1961) notes that the fines are partially bound to the coarse material by moisture bonds during wet sieving. The amount of material passing 140 mesh was increased by 4 to 10 percent for the Rocky Flats samples and 20 percent for the Trinity sample. This material was not used in the mass balances or for radiochemistry analysis.

6. The "pipet aliquoting" procedure for determining the total fraction of the sample less than 10 micrometer was incorrectly done on oven-dried samples. Thus, the results were anomolously low. The values for the total sample fraction less than 10 micrometer are therefore estimates based on multiple elutions from the settling column. Various numbers of elutions indicated values of up to 10 percent for the Rocky Flats samples. Based on the material recovered, the total value is estimated to be 20 percent.

7. The amount of the plutonium in the greater than 2-mm size fraction was not determined.

The results of the study are given in Table 13. The size fractions of less than 2 mm and 100 micrometers are based on the sample that passed 10- and 140-mesh sieves, respectively. The less than 10 micrometer size is passed on an equivalent aerodynamic diameter in air (density of 1 g/cm^3).

The Rocky Flats soil had a smaller particle size distribution than the Trinity sample. The size difference is also reflected in the distribution of plutonium. About 50 percent of the plutonium from the Rocky Flats samples was associated with the less than 10-micrometer size versus about 10 percent for the Trinity sample. The specific activity of plutonium in soil (pCi/g) appears to be generally inversely proportional to particle size. The ratio of the concentration of plutonium in the less than 10-micrometer fraction to that in the less than 2-mm fraction (basic soil size) was about 2.4 versus 1.8 for the less than 100-micrometer size fraction.

The radiochemistry results indicate good reproducibility for the preparation and analysis procedures. The only anomalous result appears to be the value of 1580 pCi/g for 1A (less than 100 micrometer). The other results for the various size fractions are within the two-sigma counting errors.

The mass fractions also show reasonable reproducibility for the sample preparation procedures. The mass of the less than 10-micrometer size fraction varies because a varying number of sedimentation runs were done for each sample. The fraction of material in the less than 10-micrometer size range is based on the maximum amount of material recovered (sample 2A) and a subjective observation that about half of the available material was recovered.

The results are compared to those of other investigators in Table 14. In general, the Trinity results for mass fractions are similar to those of Tamura (1975) for NTS (similar sandy soils). The results of Johnson et al. show reasonable agreement with the ORP-LVF results, especially considering the differences in the treatment techniques. Johnson et al. used hydrogen peroxide to

TABLE 13. SOIL MASS AND PLUTONIUM ASSOCIATED WITH VARIOUS PARTICLE SIZE FRACTIONS OF SOIL

	Mass and Activity of Material				Fraction of Material Passing 10 Mesh Sieve		
Sample and Units	Greater Than 2 mm	Less Than 2 mm	Less Than 100 µm	Less Than 10 µm	Less Than 2 mm	Less Than 100 µm	Less Than 10 µm[a]
Trinity (g)	341	1147	578	34	1.0	0.50	0.05
(pCi/g)	-	1.3 ± 0.2[b]	1.9 ± 0.10	2.0 ± 0.10		1.5	1.5
(pCi)	-	1468	1087	138[a]		0.74	0.09
Rocky Flats							
1A (grams)	133	502	188	46		0.38	0.2
(pCi/g)	-	635 ± 91	1580 ± 160	1680 ± 160		2.5	2.6
(pCi)	-	3.19 E5	2.96 E5	1.69 E5		0.93	0.5
1B (grams)	140	487	178	44		0.37	0.2
(pCi/g)	-	634 ± 94	1050 ± 130	1730 ± 190		1.6	2.7
(pCi)	-	3.09 E5	1.87 E5	1.69 E5		0.61	0.6
1C (grams)	169	568	203	20		0.36	0.2
(pCi/g)	-	593 ± 83	939 ± 113	1460 ± 160		1.6	2.5
(pCi)	-	3.37 E3	1.91 E5	1.66 E5		0.57	0.5
Rocky Flats							
2A (grams)	93	591	319	71		0.54	0.2
(pCi/g)	-	642 ± 95	1030 ± 120	1590 ± 150		1.6	2.0
(pCi)	-	3.79 E5	3.30 E5	1.88 E5		0.87	0.5
2B (grams)	88	462	213	40		0.46	0.2
	Samples not analyzed						
2C (grams)	72	490	216	38		0.44	0.2
(pCi/g)		838 ± 142	Other samples not analyzed				
Rocky Flats Average (grams)					1.0	0.43 ± 0.07	0.2[a]
(pCi/g)		670 ± 100[c]	1150 ± 300	1620 ± 120	1.0	1.8 ± 0.5	2.4 ± 0.3
(pCi)					1.0	0.75 ± 0.18	0.5

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[a] Six percent of the Trinity soil mass and 20 percent of the Rocky Flats soil mass were assumed to be in this size.
[b] Two sigma counting errors.
[c] Standard deviation.
En indicates 10^m; e.g. $E5=10^5$

TABLE 14. SOIL SIZE MASS AND ACTIVITY FRACTIONS OF VARIOUS INVESTIGATORS

Investigator	Sample Location	Fraction of Total Sample Greater than 2 mm (mass basic)	Ratio of the sample mass and plutonium concentration in the less than 2 mm fraction which was in the less than:** 100 µm fraction (mass)	100 µm fraction (activity)	10 µm fraction (mass)	10 µm fraction (activity)	Depth of sample (cm)	Ultrasonic Dispersion Used	Remarks
ORP-LVF	Trinity	0.23	0.50	1.5	0.05	1.5	2.5	No	
Tamura (1975)	NTS #1	0.20	0.34	--	0.033	--	5	No	Desert Pavement
	#1	0.20	0.40	--	0.083	--	5	Yes	Desert Pavement
	#2	0.027	0.45	--	0.011	--	5	No	Desert Mound
	#2	0.027	0.51	--	0.086	--	5	Yes	Desert Mound
ORP-LVF	Rocky Flats		0.43±0.07	1.8 ± 0.5	0.2 ± 0.1	2.4 ± 0.3	1	No	4 Samples
Johnson et. al.	RFP (4 samples)	--	--	--	0.28±0.12	5 ± 50%*	surface dust	Yes	< 17 µm, 1g/cm^3, used*
	(4 samples)	--	--	--	0.25±0.04	3 ± 25%*		Yes	H_2O_2 to break bonds
	(7 samples)	--	--	--	0.36±0.09	2 ± 40%*	surface	Yes	Dry sieved, after drying
	RFP (1 Bkgd.)	--	--	--	0.49	~6 *	dust	Yes	
Little et. al. (1973)	Rocky Flats	0.31	0.05	1.8	--	--	3		Dry sieved
	Rocky Flats	0.40	0.13	~ 4	--	--	3		Dry sieved
Tamura (1975)	ORNL	0	1	--	0.30	--	7.5	No	Flood plain silt
		0	1	--	0.38	--	7.5	Yes	Flood plain silt
Tamura (1975)	Mound Lab	0	0.87	--	0.30	--	Core	No	Silt
	Ohio	0	0.91	--	0.37	--	Core	Yes	Silt

* The Plutonium concentration in the total sample is not based on the sample of material. Rather it is based on Johnson's et. al. adaption of isopleths from Krey and Hardy (1970).

The values were estimated by dividing the average plutonium in soil concentrations, for given areas, for particles less than 5 micrometers in diameter (density 11 g/cm^3) from Johnson et al. by the plutonium concentration in the total soil estimated from isopleths that Johnson et al. adopted from Krey and Hardy (1970). The error term is the standard deviation from averaging the results.

The reference to a 17 um diameter relates to the equivalent aerodynamic diameter in air.

**Mass refers to the mass fraction of material (i.e., g/g).

Activity refers to the ratio of plutonium concentrations (i.e., pCi/g:pCi/g).

destroy any organically-bonded conglomerates, and ultrasonic mixing to further destroy conglomerate bonds. The intent of the ORP-LVF treatment was to preserve the basic conglomerates that would not disperse in a water suspension.

The results of Little et al. (1973) indicate a relatively small fraction of material in the less than 100-micrometer size class. This may be due to the difference in samples, or to oven-drying the sample (which stablizes the conglomerates) and dry sieving versus wet sieving the sample at 140 mesh.

The results of Tamura (1975) from Mound Laboratory, Ohio and Oak Ridge National Laboratory (ORNL) are for silt samples. Thus, it was expected that a large fraction of the material would pass 140 mesh.

AIR SAMPLING TECHNIQUES

Inhalation is the primary human intake pathway for plutonium; thus air sampling data are the preferred environmental data for inhalation exposure evaluation. In order to assess inhalation hazards from soil sampling, it is necessary to postulate factors for resuspension and atmospheric transport of plutonium. Air sampling provides direct evaluation of atmospheric concentrations of plutonium from airborne releases prior to deposition, and a direct measure of resuspended material. Furthermore, soil samples only provide results for discrete points within potentially heterogeneous areas--whereas air sample results indicate the average concentration for plutonium over a general area.

Air sample results are not always generally applicable to human exposure or even to actual atmospheric concentrations of the sampled material. For plutonium, the emphasis is on the particulate material. Thus, there are the concerns of:

a. Isokinetic sampling--sampling at the air stream flowrate so that the particle size distribution of the sample is representative of that in the atmosphere.

b. The air sampler face velocity or linear flowrate should be representative of human biophysical parameters. If the sampler inlet configuration and linear flowrate are not properly designed, the sampler will not obtain a sample of the representative particle-size distribution inhaled by man. Intake and deposition within the respiratory tract is dependent on the equivalent aerodynamic particle-size distribution of the inhaled material.

c. If the sampler is of the filtration type, the filtration material must be such as to provide retention of the airborne material at the sampling flow-rate. The dust-loading pressure drop characteristics of the filtering material must be considered also.

d. The sampler must be properly located so that it obtains a representative sample of the atmosphere, i.e., not on the leeward side of buildings or hills.

Given the above comments, it becomes apparent that a random air sample does not necessarily provide all necessary hazard-assessment information. Sampling parameters must be defined.

There are several reference works on aerosol-sampling technology (Mercer, 1973). Thus, this section will not attempt to discuss the physics of aerosols. This section will focus on aerosol-sampling techniques pertinent to assessing airborne concentrations of plutonium. The emphasis will be on techniques designed for adequate flowrates and sampling times for assessing environmental concentrations (less than 0.1 fCi of plutonium per cubic meter of air). A minimum detection level of about 20 fCi is required on the final separated sample. Assuming a chemical yield of 50 percent, and given the uncertainties in sample analysis, a reasonable minimum required activity in the sample is 80 fCi. The necessary sampling rate is equal to the minimum required sample activity divided by the product of air concentration and sampling time. Thus, assuming an air concentration of 0.05 fCi/m^3, a sample volume of 1600 cubic meters is necessary. Therefore, for a flow-rate of one cubic meter per minute, the sampling time required is 1600 minutes, or about one day.

Work by Bagnold (1954) and Chepil and Woodruff (1963), referenced by Anspaugh et al. (1975) and Buck et al. (in press), indicates that saltation and surface creep account for the majority of airborne soil movement. These processes generally include soil particles from 50-500 micrometers and 500-2000 micrometers, respectively. Thus, although these processes generally move particles near the ground (within one meter), air samples should be scrutinized to insure that they do not contain large amounts of material above the respirable particle-size range (5 to 10 micrometers).

The phenomona of resuspension is generally related to particles ranging up to 50 micrometers. Thus, only a fraction of windborne material related to resuspension is respirable, and resuspension accounts for less than 10 percent of airborne soil movement.

PHYSICAL CHARACTERISTICS OF AEROSOLS

The physical characteristics of airborne particles are generally described by their aerodynamic characteristics. In simple terms, the forces acting on a particle are proportional to the density of the particle and the square of the diameter of the particle for particles of the density and diameter of interest for plutonium inhalation (Mercer, 1973; Morrow, 1966; and ICRP, 1972).

Deposition of plutonium-related particles greater than 10-micrometer aerodynamic diameter in the pulmonary section of the lungs is essentially zero (Mercer, 1973 and Morrow, 1966). The aerodynamic diameter relates to the equivalent diameter of a particle with a density of 1 g/cm^3 which responds similarly in air streams to the subject particle.

The terminal setting velocity of a particle can be described as (Eisenbud, 1963):

$$V = 0.003\ \rho d^2$$

Where V = velocity (cm/sec)

ρ = density of particle (g/cm^3)

d = particle diameter (μm)

This equation is applicable for particles with streamline motion (e.g., density less than 10 g/cm^3 and diameter less than 50 μm or d less than $115/\rho^{1/3}$). When the diameter of a particle is less than the mean free path of gas molecules, Stokes' equation underestimates the terminal settling velocity. This can be corrected for by using Cunningham's modification of Stokes' equation (Eisenbud, 1963):

$$V_c = V_s[1 + (1.7\lambda/10^{-4}d)]$$

Where V_c = corrected velocity

V_s = Stokes' Law velocity

λ = mean free path of gas molecules, about 10^{-5} cm at sea level.

d = particle diameter, μm

The air entering the nose is actually deficient, with respect to the ambient air, in particles having settling velocities similar to the inhalation face velocity and normal wind speeds. (ICRP, 1966). The inhalation face velocity is (ICRP, 1966):

$$1500 \text{ ml} \times \frac{15}{\text{min}} \times \frac{\text{nose}}{1.5 \text{ cm}^2} \times \frac{\text{meter}}{100 \text{ cm}} \times \frac{\text{min}}{60 \text{ sec}} = 2.5 \text{ m/sec}$$

The assumptions are:

a. Tidal or inspirational volume, 1500 ml

b. Inspiration rate, 15 per minute

c. Cross sectional area of nostril, 0.75 cm^2 or 1.5 cm^2 for nose.

The above parameters correspond to a reasonable level of activity, somewhat equivalent to industrial workers. Basal metabolism is about 500 ml tidal volume with 12 respirations per minute (Comroe et al., 1963). Mild to moderate activity would relate to 750 cm^3 and a respiration-rate of 15 per minute (ICRP, 1966).

Air sampler face velocities vary over a wide range. A volume of 1 l/min for a 1 cm diameter filter (0.785 cm^2) relates to a velocity of 0.21 m/sec (1 ft^3 /min through a 1- in diameter filter is 0.93 m/sec). Thus, for a nominal high volume sampler (1 m^3/min for an 8 by 10 inch filter having an effective filter area of 7 by 9 inches), the face velocity is 0.41 m/sec. If a 4 in-diameter filter was used, the velocity would be about 2 m/sec.

A nominal wind velocity of 10 miles per hour is 4.47 m/sec. Thus, it becomes apparent that it is difficult to sample isokinetically with conventional filter-type samplers. The high volume sampler only has a face velocity of 2 m/sec with a 4 in-diameter filter. Even the face velocity for the human nose is about 2.5 m/sec, or the equivalent of 5 miles per hour.

Patty (1958) indicates that the air velocity drops to about 10 percent at one diameter from the face of an exhaust vent. Thus, given the ratio of the diameters of air samplers and human nostrils (generally 10 cm versus less than 1 cm, respectively), air samplers with face velocities 0.25 m/sec generally should be equivalent to the human nose. Furthermore, the settling velocity of a 10 μm aerodynamic equivalent particle is only about 0.3 cm/sec; i.e., two orders of magnitude less than a sampler face velocity of 0.25 m/sec.

The above does not resolve the problem of subisokinetic sampling rates. If the sample face is oriented downwind, there is a definite probability of unrepresentative sampling due to an inadequate capture velocity. Sehmel (1973) has generally resolved this problem by placing samplers on a pivot. The sampler orientation is then controlled by a wind-oriented cowl, so that the sampler is oriented into the wind.

TYPES OF AIR SAMPLERS

There are several techniques for obtaining samples of the particulate material suspended in air. They include:

1. Mass air samplers where the air stream is drawn through a filter medium.

2. Electrostatic precipitators where the particulates are removed from the air stream by electrostatic force.

3. Impactors which normally are used to segregate the particulates into various size categories. Particulates are impacted on various stages (size categories) as a result of channeling the air stream around the impaction plane.

4. Air elutriation sampling techniques separate particles on the basis of the settling velocity. The differential of the settling velocity and the velocity of the air current in which the particle is moving is used to separate particles based on their size and density.

5. Aerosol centrifuges utilize the same principle as elutriators, except centrifugal force is used in place of gravitational force.

Many samplers utilize several of the techniques. Andersen impactors use several impactor stages to segregate particles into size fractions from 1 or 2 to 10 micrometers and a filter to collect the smaller particles. The sampler may be designed to exclude material over 10 micrometers. Some characteristics of the various types of samplers are discussed below.

Mass or Filter-type Air Sampler

An air mover is used to draw air through a fibrous or membrane-type filter. Although particle sizing can be done either through optical or audioradiographic techniques, or by using filter packs containing filters with different size penetration characteristics, normally particle sizing is not done for filter-type samples.

Filter-type samplers come in a large range of sizes; from personnel monitoring devices having flowrates of liters per minute, to the high volume samplers at about 1000 liters per minute. Anspaugh et al. (1974) report on an ultra high volume sampler capable of flowrates of 25,000 liters per minute. This sampler was designed to obtain samples of resuspended dust over short periods of time.

The principal parameters for filtration-type samplers are the flowrate, face velocity, and the filtering medium. The flowrate determines the volume of air sampled per unit time and, thus, in part, dictates the sampling time, assuming the amount of material collected is near the MDA. The face velocity affects not only the characteristics of the aerosol drawn into the sampler, but also the fraction of material collected by the filter. The decision concerning filtering material must be based on face velocity, expected dust loading, proposed analytical techniques, particle size retention requirements, and pressure drop characteristics.

Electrostatic Precipitation

This is a two-stage process. First, the particles must be charged in a unipolar ion field. In the second stage, a strong electric field is used to precipitate the charged particles on a suitable collection surface (Mercer, 1973). Collection efficiencies of 99.9 percent can be obtained for particles of 0.2 to 0.7 micrometer mass median diameter; whereas particles around 0.2 micrometer are difficult to collect because of the small charge retained by the particle. Because of design complexities and power requirements, electrostatic precipitators are not used commonly in environmental sampling.

Recently, the U.S. Environmental Protection Agency laboratory at the Research Triangle Park in North Carolina has participated in the development of an ultra high volume sampling system. The system is capable of flow-rates of 26 m^3/min. The particulate material is segregated into respirable and non-respirable material by use of an electrostatic precipitator and other techniques.

High-Volume Cascade Impactors

Cascade impactors are composed of a series of impactor stages and a final filter. The units of interest generally provide several fractional steps for particles between 1 and 10 micrometers in diameter, with the final filter collecting material less than 1 micrometer in diameter. Cascade impactors have demonstrated their ability to provide particle-size distributions, based on the equivalent aerodynamic diameter, for ambient levels of airborne particulate material.

A single impaction stage is composed of a plate with precision-machined orifices followed by an impaction plate. The impaction plate contains the orifices for the next stage. The airstream flows through the orifice, and as it is impinged on the impaction plate the airstream splits to go on through the adjoining orifices. The inertial qualities of the particles cause those in the designed size spectrum to be impacted on the impaction plate, directly below the orifice. The deflected airstream goes through the adjoining orifices. The orifices are of a slightly smaller diameter than the previous stage. Thus, the constant air volume, but smaller orifice diameter results in an increased air velocity, with the resulting impaction of the next size smaller particles on the following impaction plate.

Mercer (1973) presents a detailed account of the theory of impaction units. There is not a discrete cutoff of particle size increments with each stage. Mercer (1973, Figure 6.36), illustrates the general fractionation that occurs. The hypothetical aerosol is assumed to be made up of unit density particles with a geometric mean diameter of 10 micrometers and a geometric standard deviation of 2. The effective cutoff aerodynamic diameters (ECAD) are 16, 8, 4, and 2 micrometers.

It generally is assumed that all particles collected on a given stage have aerodynamic diameters larger than the ECAD for that stage. A stage not only does not collect all particles above the ECAD, but collects some particles smaller than the ECAD. Some material is assumed to be collected that is not collected, and some material assumed to be passed by a stage is actually retained. These are about equal for each stage. Thus, the actual mass per stage is approximately correct. The differences in the mass for a stage generally are less for round jets than for rectangular jets (Mercer, 1973, p.234). The ECAD is the diameter for a particle which has a 50 percent probability of retention on the subject stage.

In addition to errors resulting from non-ideal design there are several potential sources of error. These include wall loss of material, disaggregation of particles, and rebound and re-entrainment of deposited material.

Wall losses refer to the retention of impacted material in the impaction stages other than at the intended impaction area. Mercer (1973, p.235) reports wall losses ranging from 14 percent to 2 percent for high sample volumes for a low volume sampler (i.e., 0.05 to 0.15 l/min).

Wall losses result from non-laminar flow between the stages. However, the wall losses can be extenuated by rebound and/or re-entrainment of the impacted material. Mercer(1973, p.236) notes rebound is a serious problem if the collection surfaces are not coated with a soft layer to cushion the impact of particles (e.g., if the impactor plate is used as the collection medium versus using a filter for collecting the impacted material). He also notes that both rebound and re-entrainment put an upper limit on the amount of material that can be collected on a stage without degrading the operation of the instrument.

Sehmel (1973) defines wall loss as the amount of material associated with the walls directly above the stage of interest, divided by the amount of activity on the stage of interest. He reports wall losses for the Andersen 2000, Inc., Model 65-100, 20 ft^3/min, high volume unit for stage loadings between about 50 and 200 mg. The losses vary from about 1 percent at 50 mg/stage to 5 to 20 percent at 200 mg/stage.

Sehmel (1974) provided additional information on the wall losses for the Andersen 2000 Inc., unit. He noted the following:

1. There appears to be no direct relationship between interstage losses and stage loading.

2. The data indicate wall losses of up to 20 percent. Operations during dust storms would undoubtedly result in higher wall losses.

3. The average particle size in the interstage material (wall loss) for each stage was much larger than should have been present for the respective stages. Apparently, some nonrespirable particles work their way through the various stages. This tends to give results that are conservative (i.e., there is more respirable material indicated as being present than actually is present in air).

There appear to be only two high-volume impactors available through commercial sources. The Andersen 2000 Inc. is based on 20 ft^3/min flow rate (566 l/min). The unit has four stages with cutoffs at 7.0, 3.3 , 2 , and 1.1 micrometers, with a backup filter for material less than 1.1 micrometers (Burton et al., 1973). The unit is about 30 cm in diameter and can be matched to high-volume air samplers. The operation of the unit has been reviewed by Burton et al. (1973) and Sehmel (1973, 1974). In addition to the previously indicated information, Burton et al. (1973) note that some types of fiberglass filters are prone to absorb atmospheric acid gases. Thus, the total mass amount of collected material cannot be directly related to a mass air sample result for a single sample. Apparently, fiberglass filters with a pH adjusted to 6.5 largely resolve the problem.

Tech Ecology, Inc. markets a 5-stage cascade impactor designed for a flow rate of 40 ft^3/min (1,130 l/min). Tech Ecology model 252 has size cutoffs of 8.2, 3.5, 2.1, 1.0, and 0.5 micrometers, with a final filter for less than 0.5 micrometers. The unit is rectangular and fits the standard 8 x 10-inch high-volume filter holder. The impactor orifices are rectangular slits 12.5 cm long. An advantage of the design is the small amount of filter paper (about 170 cm^2) that has to be analyzed for results from each stage. There appear to be no published reports evaluating this unit.

Sehmel (1973) reports results of a study with the impactor facing into the wind, and with the impactor face pointed vertically up or down. About 50 percent more material was collected with the sampler pointed up versus down. The results with the sampler oriented into the wind, with a wind directed cowl, fell between the upward and downward oriented sampler, and were considered to be the most valid of the three sets of results. The data were obtained using Andersen 2000 Inc. samplers. The flowrate was 20 ft^3/min (570 l/min), and the linear velocity for the 6-in (15-cm) diameter cowl was 0.54 m/sec (1.2 miles/hr).

Air Elutriator and Centrifugal or Cyclone Samplers

Air elutriators and cyclones utilize similar processes. The settling velocity of the particle is used to fractionate material in elutriators, whereas cyclones utilize centrifugal force concepts. Both systems generally are used in two-stage samplers. The elutriator and cyclone stages are used to remove the non-respirable material from the air stream. The respirable material (less than several micrometers in diameter) is collected on a filter in the second stage.

The fractionated particulate material passed by the cyclone generally relates to the definition of respirable material designated as the Los Alamos Scientific Laboratory (LASL) criterion. The horizontal elutriator passes material which relates to the criteria of the British Medical Research Council (1961). The LASL criteria resulted from a meeting called by the Atomic Energy Commission, Office of Health and Safety, at Los Alamos in 1961. Thus, the term AEC criteria is also used. The American Conference of Governmental Industrial Hygienists set forth a slightly revised version of the LASL criteria (Federal Register, 1969). These criteria, are summarized by AIHA (1970) and Ettinger et al. (1970).

Air elutriation is a process of particle separation based on the settling velocity of the particle. This process may be done on either a horizontal or vertical plane--thus horizontal or vertical elutriators. Both techniques are based on the comparison of particle settling velocities and the velocity of the air stream transporting the particle.

In vertical elutriators, the particles are carried upward in a diverging air stream until they reach a point in the air stream at which their settling velocity equals the vertical component of the diminishing air velocity. Vertical elutriators have been used for size-fractionation of powders, but have received little use as air samplers (Mercer, 1973, p. 192).

In horizontal elutriators (HE), the particle settling velocity is normal to the transporting air velocity. The air stream passes through a horizontal duct. The distance from the duct inlet at which particles fall out is inversely proportional to their settling velocity or aerodynamic particle size. The size distribution of material along the path length of the duct varies, thus indicating the potential for obtaining an indication of the size spectrum.

The vertical dimension of the inlet air duct of a HE is generally a significant fraction of the total vertical fall height. Thus, particles entering at the lower level of the duct have a reduced fall height, compared to particles entering the upper part of the duct. Thus, there is a general spread of the

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The vertical dimension of the inlet air duct of a HE is generally a significant fraction of the total vertical fall height. Thus, particles entering at the lower level of the duct have a reduced fall height, compared to particles entering the upper part of the duct. Thus, there is a general spread of the size distribution along the horizontal length of the HE. Mercer (1973) indicates that a sharp cutoff can be obtained with a properly designed HE. Wright (1954) indicates the comparison of the actual and theoretical retention values for the 100 l/min Hexhlet instrument. The following retention values generally are obtainable (Wright, 1954; AIHA, 1970; and Mercer, 1973):

Particle Size (micrometers)	Percent Retention (In HE)
1	~2
<2	10
5	50
7	100

Lippmann (1970) describes various HE's. Although most of the units operate in the liter-per-minute category, Wright (1954) presents data on the Hexhlet unit, designed for 100 l/min. The design was subsequently revised to 50 l/min. Shanty and Hemeon (1963) discuss a unit designed for a flowrate of 1250 l/min.

Lippmann (1970) notes it is generally difficult to collect the material from HE units for analysis. In many designs, it apparently is difficult to clean the HE adequately, to prevent future samples from being contaminated by re-entrained material. A preference for cyclone separators is noted.

Centrifugal or cyclone samplers (CS) separate particles based on their centrifugal force (i.e., mass and diameter, or equivalent aerodynamic diameter). They are more flexible than HE's in that they can be operated in any position. Thus, small cyclones have been developed as personnel monitors. Lippmann (1970) indicates a listing of CS's, most of which are in the liter-per-minute flowrate range, although one unit with a turbine blower is rated at about 1000 l/min. Volchok et al. (1972) report results from the Rocky Flats, Colorado area using a 100 l/min CS described by Lippmann and Harris (1962).

The design parameters on a CS are critical. Ettinger et al. (1970, Table 4) indicates the change in the cyclone retention with flowrate for a one-half inch unit. Lippmann (1970) reports that most of the cyclone calibrations prior to about 1970 were in error. The errors were due to an overestimate of particle sizes, as a result of the microscopic measurement technique used. Apparently the disagreements range up to a factor of two in flowrate for describing a given size cutoff. Given this, the data presented by Ettinger et al. (1970, Table 4) would indicate roughly up to a factor of two error in cyclone retention for 2-micrometer particles.

Combination Electrostatic Precipitation and Cascade Impaction

Henry and Mitchell (1975) present data on a high-volume sampler developed for EPA, Research Triangle Park, North Carolina. The sampler is designed for 28 m^3/min (1000 ft^3/min). It contains impaction stages designed for particles greater than 3.5 micrometer and 1.7 to 3.5 micrometer. The final stage, for less than 1.7 micrometer particles, is an electrostatic precipitator. There does not appear to be any published information evaluating the operation of the unit.

TYPES OF FILTRATION MATERIAL

Many of the characteristics and limitations of filtration samplers relate to the filter medium. Based on their physical structure, filters can be classified as either fibrous mats or porous membranes. Filters have varying particle size retention characteristics, and the characteristics of a given filter are dependent on the airstream face velocity. Other considerations include dust loading and associated pressure drop, and the presence of trace materials (e.g., uranium, thorium, and radium) in the filter material.

The theory of fibrous mats is discussed by Mercer (1973, p.115). Fibrous filters are made of cellulose fibers, plastic fibers, glass fibers, and other materials including asbestos. The filter performance is closely related to the diameter of the fibers, with the smaller diameter fibers having better collection properties. Collection of particles on filters is not solely a sieving phenomena; rather, it is due to electrostatic forces, interception, impaction, and diffusion.

Most common filters, fibrous or membrane, have adequate particle collection efficiencies for air sampling; however, it has been noted that Whatman 41 cellulose fiber filters have a fairly low efficiency (70 to 80 percent) at low face velocities of 20 to 30 ft/min (about 0.13 m/sec or 0.28 mi/hr). This is equivalent to a flowrate of about 2 ft^3/min (60 l/min) through a 4-inch (10-cm) diameter filter.

Unpublished information from a study by Eadie, ORP-LVF provides data on the dust loading and pressure drop properties of several filters. Tests were conducted on 4-in (10-cm) diameter Whatman 541, Acropor, Gelman Type E Glass Fiber, and Microsorban filters at initial flow rates of about 10 ft^3/min (280 l/min). The results indicate that the glass fiber and Microsorban filters had better dust loading properties than the other filters. Glass fiber filters showed a 30 percent decrease in flow rate with a filter load of 260 mg. Microsorban indicated less than a 10 percent decrease in flow rate with a load of 200 mg, the highest load used on the Microsorban tests. Conversely, Whatman 541 paper indicated a 60 percent flow rate decrease with a dust load of 200 mg or less.

The filter composition affects the difficulty and precision of radiochemistry analysis. The ease of wet or dry ashing Whatman paper always has made it a favorite with chemists. The difficulty of dissolving fiberglass filters and the associated trace elements put in solution have provided difficulty for radiochemical analysis. Even with refined techniques, the EPA's Las Vegas analytical laboratory has found about 80 in^2 (500 cm^2) to be the maximum amount of fiberglass material to be amenable to plutonium chemistry analysis.

Microsorban, a polystyrene fibrous mat material, is very amenable to radiochemistry. If dried and heated for several hours at increments of 100°C to 350°C, it can be white-ashed to a powder at 600°C. When put in solution, it essentially has zero residual (Golchert, Argonne National Laboratory, Personal communication, Feb. 1975).

Filtering materials contain numerous trace elements. These elements include uranium and thorium progeny, and many metals (especially in the fiberglass filters). The amounts and variances of the trace elements significantly effect the sensitivity of monitoring low levels of these trace elements in air. Table 15 indicates values determined by ORP-LVF for some of these contaminants in several filters.

The analyses for many of the radionuclides are incomplete. However, it is evident that most of the filter materials contain varying amounts of radium-226, uranium and thorium. Admittedly, some of the variation may be due to analytical or counting error, but many of the results were based on a composite of four filters.

Golchert, in a private communication on Feb. 11, 1976, noted that Argonne National Laboratory has detected concentrations of 4 to 18 fCi of thorium-232 and 2 to 8 fCi of uranium-238 per 780 cm^2 of Microsorban. These relate to average values of about 1 fCi and 0.5 fCi, respectively of thorium-232 and uranium-238 (1 fCi total uranium) for a 4-inch diameter (10-cm) Microsorban filter. These values are significantly lower than the radium-226 values given in Table 15.

Given several assumptions, these trace contaminants can be related to equivalent air concentrations. Assuming a sampled volume of 2000 m^3 (1.4 m^3/min for 1 day), a contamination level of 0.2 pCi/filter is equivalent to an air concentration of 0.1 fCi/m^3. This is about one-fifth of the nominal radium-226 ambient concentrations (see section on natural activity).

TABLE 15. RADIONUCLIDE LEVELS IN AIR FILTERS (ORP-LVF)

Filter Material	Number of Samples	Weight		pCi per Filter							
				Ra-226		U-238		Th-230		Th-232	
		Ave. (g)	Range	Ave	Range	Ave	Range	Ave	Range	Ave	Range
Whatman 41	4	0.62	1.06	0.16	1.82						
Whatman 541	2	0.62	1.01	0.30	1.28						
Gelman Glass Fiber	7	0.52	1.04	0.26	1.96	0.085	6.15	0.18	1.63	0.013	2.00
Microsorban	5	1.47	1.05	0.17	3.73						
Acropore	5	0.41	1.02	0.90	5.7						
Millipore	1	1.7	----	0.1	---	<0.01					

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* The range is the ratio of the highest result to the lowest result.

There appears to be minimal, if any, plutonium contamination in air filter materials. Thus, these contaminants are somewhat academic for sampling related solely to plutonium. But their presence should be recognized in determining methods for plutonium analysis and when considering gross alpha measurements.

The variance of filter weights has to be recognized if the specific activity of the material on air samples is to be determined. Mercer (1973) notes that cellulose fiber filters are prone to collect moisture from humid air. At 100 percent relative humidity, a cellulose filter may gain 17 percent weight, compared to its dry weight, versus 0.1 percent for fiberglass filters.

AMBIENT CONCENTRATIONS OF NATURALLY-OCCURRING ALPHA EMITTERS

The ambient concentration of plutonium-239 in air is roughly 30 aCi/m^3. This is significantly below the standard concentration guide of 10 CFR 20 for individuals in the general population which is 60,000 aCi/m^3.

Ambient concentrations of the naturally- occurring alpha emitters range over several orders of magnitude. Values vary from yearly averages of 100 aCi/m^3 of total uranium, about 30 aCi/m^3 of thorium-238 and 232, and 50 aCi/m^3 of thorium-230 (AEC, 1974a) to 2000 aCi/m^3 of polonium-210 (AEC, 1973a).

Based on information in the previous section, roughly 100 aCi/m^3 of the various nuclides could be accounted for by contamination in the filter material, depending on the filter material used and volume of air sampled per quantity of filter material.

By way of illustration, the total gross alpha activity on an air filter result could be roughly 0.9 pCi under the following conditions . Assuming a sampling rate of 1 m^3/min, a sampling time of 100 minutes, and an estimated nominal ambient background of 4000 aCi/m^3, the gross alpha value is comprised of 0.5 pCi from natural contaminants in the filter and 0.4 pCi of activity collected during the sampling period.

The gross alpha estimate is somewhat greater than the average gross alpha estimates from Argonne National Laboratory (ANL), Illinois, 2,500 aCi/m^3 (AEC, 1974a); Rocky Flats, Colorado, 5,000 aCi/m^3 (AEC, 1973a); and Los Alamos, New Mexico, 1,000 aCi/m^3 (AEC, 1973a). The above gross alpha results are based on longer run times (days); thus, the filter contamination becomes less significant (estimated at 5,000 aCi/m^3 in our hypothesized value). Also, the ANL and Los Alamos results are based on Microsorban filter material, which has a contamination value lower than the postulated value. In addition to these factors, the hypothesis of the gross alpha air concentration was based on higher-than-normal values of natural radionuclides in the atmosphere. Even with the noted conservative assumptions, the postulated ambient gross alpha estimate of 9,000 aCi/m^3 is significantly below the plutonium-239 concentration guide of 60,000 aCi/m^3.

ANALYSIS OF AIR SAMPLES

Analysis of air samples generally is equivalent to the analysis of soil samples, plus considerations of the sampling medium if a filter is used. The medium generally does not present unusual problems, except in the case of fiberglass filters. Most membrane filters, Microsorban, and cellulose fiber filters generally can be wet or dry ashed to a low residual. The specific activity of naturally occurring uranium and thorium radionuclides in air samples generally is similar to their specific activity in soil (Golchert, ANL, personal communication, February 1976).

Plutonium in air samples stems from both resuspended soil and fallout. In areas with an air concentration of about 30 aCi/m^3 from atmospheric fallout and deposition on the soil of less than 10 - 30 nCi/m^2 (i.e., about 10 times background), the plutonium concentration in air is largely a result of atmospheric fallout.[a] Thus, the particulate material on air filters has a higher specific activity than that in soil. The information on sample analysis in the following section is applicable to air samples.

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[a] Douglas, ORP-LVF personal communication, February 1976 and A. Hazle, Colorado State Department of Health, personal communication, February 1976.

G. Merrill (Air Force McClellan Central Laboratory, verbal communication, May 3, 1976) indicated that using plutonium isotopic ratios from mass spectrometry, a contribution from resuspended Trinity contamination (up to tens of percent) could be detected in the data from Douglas.

SAMPLE ANALYSIS TECHNIQUES

In many situations it appears that the analysis of samples is not integrated with the philosophy of collection of the samples and the objectives of the overall program. Plutonium in soil, as well as in other media such as animal tissue, exemplifies this situation, because of its potentially heterogeneous distribution. The objectives of the program may dictate compositing up to ten discrete soil samples, to insure a sample representative of the sampled location. The total sample, composed of several kilograms, may be milled and mixed, with only a small aliquot taken for the actual analysis. This aliquot may vary from as small as one gram (EMSL-EPA, Las Vegas prior to January 1975) to about 100 grams (Krey and Hardy, 1970). The aliquot size for analysis is related to the difficulties of dissolution of large quantities of soil, and for fusion techniques the limitations and costs of the required analytical apparatus.

In most instances, the analyst follows the philosophy of taking an aliquot which he thinks can be adequately analyzed. The potential presence of discrete particulate plutonium in the sample, and the probability of obtaining a representative fraction of the material in the aliquot, may not be addressed.

The problem of adequate sample size also relates to some biological samples, such as bovine livers, kidneys, and bones, etc., where it may not be convenient to analyze the whole sample. Consideration of the heterogeneous structure of organs is necessary if analyses of aliquots of the organs are to be meaningful.

ANALYTICAL SENSITIVITY

Analytical sensitivities are generally related to the counting error (Johns, 1975; Sill, 1971; Krey and Hardy, 1970; Chu, 1971; and Eberline, 1974). In many instances, the minimum detectable activity (MDA) is defined as a value which is equal to the 2-standard deviation (SD) or 95 percent confidence level (C.L.) value (e.g., 20 fCi ± 20 fCi). Such results are normally presented as less than values (e.g., <20 fCi).

The use of a value of less than the 2-SD value results in the significant probability of an erroneous statement. If one believes in the validity of the counting error, there is only a 50 percent probability that the value is less than the 2-SD value (e.g., <20 fCi). In order to have a 95 percent confidence level statement, a value of the mean plus 2-SD should be used.

Eberline Instrument Corporation (1974) uses another fairly standard technique of three times the background counting error. This gives an MDA somewhat less than the 2-SD equal to the mean technique. But, as in the 2-SD technique the statement of a less than value has a 50 percent or greater probability of being in error.

Robinson et al. (1975) considered the range of background samples for plutonium-238 and the variation of results for low concentrations. The objective of the study was to assess the inventory above the baseline or background level near the Mound Laboratory, Miamisburg, Ohio. Aliquots of a sediment sample from 50 miles upwind of the plant were used for background determinations. The reported gross concentrations in the background samples (no system background subtracted) ranged from 0.000 to 0.765 pCi/g with a mean of 0.077 ± 0.040 (1-SD for 50 values). The minimum detectable level was set at 0.1 pCi/g. Using 0.1 pCi/g and recognizing that background values ranged up to 0.8 pCi/g, the sample results were reported as less than 0.1 pCi/g or the actual result for values above 0.1 pCi/g. Blank background values were not subtracted from the results. Actual plutonium-238 background values for this area were reported to be 0.0002 pCi/g for 30 cm (12 in.) depth cores, or roughly 0.002 pCi/g for the top 5 cm (2 in.).

Although the results of Robinson et al. are not directly applicable to studies at background levels, the concept of using the variation in low level results, versus the counting error, to define the MDA has merit.

The sensitivity of analytical procedures is inherently a function of five parameters, some of which are reasonably fixed, but several of which can be varied. The parameters are:

1. Sample size: The sensitivity depends on the total amount of activity present. Thus, ideally the sensitivity of a 10-gram sample is one-tenth of that for a 1-gram sample. The acid dissolution and fusion techniques tend to have a nominal maximum of about 10 grams of sample. The ease of analysis, size of vessels and quantities of interfering elements generally result in the analysist's preference for a sample smaller than 10 grams. The size refers to the dry weight of soil, or weight of ash for biological samples.

2. Radiochemical yield: The yield is not an independent variable. Mullins (EMSL-LV, verbal communication, Feb., 1975) noted that although yields of 90 percent plus were obtainable with 1-gram soil samples, the yield for 10-gram samples had been about 50 percent,

although there was hope for improving it. The drop in yield is due to the interference from the increased quantities of elements such as calcium and iron. Thus, the 10-gram samples are only the equivalent of 5-gram samples, or less, but there is still the benefit of obtaining a more representative aliquot. There is an additional uncertainty with low yields, due to the uncertainty in the yield determination. A measured recovered activity divided by a yield of 90 percent (with an uncertainty of 10 percent) has a much lower uncertainty than a value divided by 50 ± 10% or 20 ± 10%. There is the additional uncertainty related to the conventional propagation of error techniques (Parrott, 1966 and Pugh and Winslow, 1966). The simple technique for the square root of the sum of the squares of the coefficient of variation only applies for the division of parameters if the coefficient of variation is at most 20 percent, and preferably less than several percent. If the error term for the denominator is large, the limits are much more difficult to calculate, and they are not symmetrical around the mean (Finney, 1971).

3. Counting efficiency: Optimally 50 percent for 2π geometry, but generally about 20 percent for alpha spectroscopy.

4. Background counting rate: The background error and sample counting error are propagated by the square root of the sum of the squares. The background for alpha spectroscopy is generally low (counts per hour or less) and stable enough that backgrounds and/or blanks are only run about once a week or less. Thus, there is the potential for actual errors in the blank count that is used to correct the sample gross count to a net count, if the chamber is contaminated.

5. The counting time for both the sample and background or blank impacts the sensitivity as a result of the counting error calculation. The counting error or standard deviation is generally assumed to fit the normal distribution with the variance equal to the total counts (i.e., standard deviation equal to the square root of the total counts). Thus, doubling the counting time reduces the percentage counting error by the square root of 2 (100 counts ± 10, versus 200 counts ± $10\sqrt{2}$). Counting times for low-level alpha analyses are normally 1000 min. (Johns, 1975).

Most calculations of counting error and thus statistics (e.g., Johns, 1975) assume the applicability of the normal distribution. Nuclear disintegration or counting statistics are basically described by the binominal distribution (Evans, 1955, and Jarett, 1946). It is only through generalizations and assumptions that the normal distribution is applicable. The basic assumption of concern for low level determinations of long half-life radionuclides is the accumulation of sufficient counts for the transition from the Poisson to the normal distribution. The minimum value normally stipulated is 20 counts, below which the Poisson is too skewed to be approximated by the normal (Evans and Jarett). Jaffery (1960) stipulates a value of 100 counts.

For a mean of 20 counts, the mode of the Poisson is 19 versus the mean and mode of 20 for the normal (Jarett, 1946). Figure 3 is a cumulative frequency plot for a mean of 10 events. The cumulative 50 percent point for the Poisson is about 9, versus 10 for the normal distribution.

Most of the minimum detectable activities (MDA)* are associated with net sample counts of about 10 above a background count of 0 to 5 - where both counting times are about 1000 minutes.

Equation 1 indicates the calculation for the probability, P, of x events occurring for the Poisson distribution, where m is the true value

$$P(x) = \frac{m^{x} \exp\text{-}m^{**}}{x!} \qquad (1)$$

Equation 2, using the same nomenclature, indicates the probability P (x) for the normal distribution

$$P\ (x) = \frac{1\ \exp\text{-}(x-m)^2/2m}{(2\ \pi m)\ 0.5} \qquad (2)$$

For an assumed mean or true value of m = 2, the probability of occurrence of a value of two is similar for the two distributions (i.e., 27.4% for the normal, versus 27.1% for the Poisson). But, the probability values of one or three occurring differs by about 20 percent for the two distributions (the values for the normal distribution are integrated between x plus and minus one-half).

It is difficult to assess the full impact of the limitation of the assumptions in using a normal distribution. But for samples near the MDA, if results related to counts of 10 or less events are used, it appears that the errors in the counting error statements and in actual results could be several tens of percent,

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* For these purposes MDA is used as a general term to indicate the defined detection limit. No attempt is made to distinguish between the original sample, a prepared sample, or curies versus counts.

** $\exp\text{-}m = e^{-m}$.

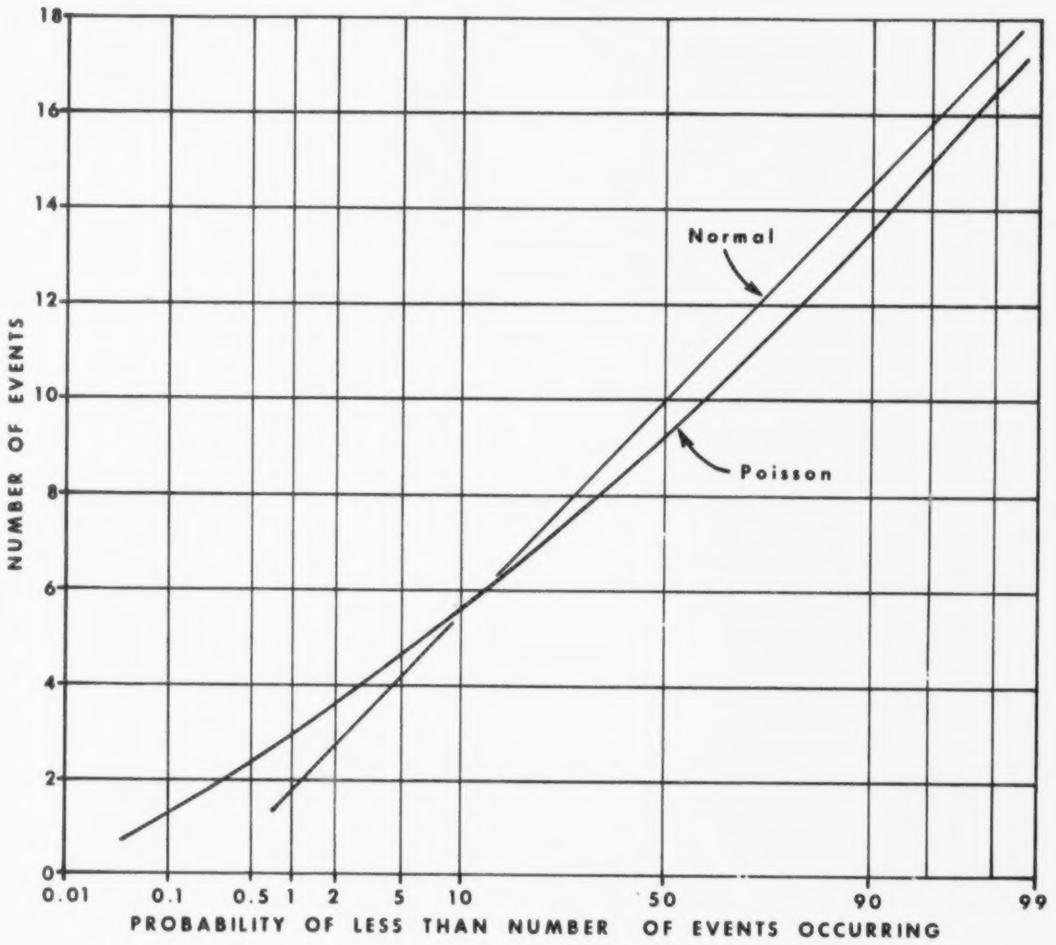

Figure 3. Cumulative frequency plot for a true value of 10.

Johns (1975) presents equations for calculating the plutonium-239 activity in a sample and the associated counting error. The calculations use the ratio of the plutonium-236 tracer added to the sample to the recovered plutonium-236, rather than an actual detector efficiency.

The counting error equation is a propagation of error of the square root of the sum of the squares of the coefficients of variation for the following parameters:

- Sample count for plutonium-239

- Reagent blank count for plutonium-239

- Sample count of plutonium-236 tracer

- Reagent blank count for plutonium-236 tracer

This results in a rather complete analysis of the counting error for a sample. For samples near the MDA, the sample count is probably around 10, and thus has the previously noted limitations of not being normally distributed. The same is true for the background or blank count for all analyses. Thus, the error term may not be truly representative by up to tens of percent for the two values.

In talking to personnel from various laboratories, it was discovered that some do not subtract an instrument background and few subtract a reagent blank background. The significance of errors associated with these practices depends on the level of sample activity, as well as the degree of possible contamination of the counting instruments, reagents, laboratory glassware, and tracer solution. Given the potential for errors, it is prudent not only to subtract background, but also to run reagent blanks containing the tracer, and use this blank as the background.

A general review of the effects of various actual numbers would indicate a potential for a misrepresentation of the error term by up to 30 percent for values near the MDA (assumed to be about 10 counts). The calculations indicate a nominal MDA of about 20 fCi/sample; assuming 1000-min count time, high chemical yield (about 90 percent), and low background (0-5 counts in 1000 min). Consideration of the assumptions indicates that the actual MDA varies from sample to sample, if it is based on counting error. Thus, single values are only nominal estimates based on representative results.

Sill (unpublished document) presents a counting error evaluation which includes several additional factors. Although Sill included error estimates for the tracer standardization and for correcting the tracer for decay since standardization, these errors are a small part of the total error. The error associated with the sample count accounts for well over 90 percent of the total error for his estimate. Furthermore, the potential error of assuming the background is zero overshadows the contributions from these other errors.

MDA's from several organizations are summarized in Table 16. Many authors do not report MDA's, and many that do, report them in terms of their specific sampling and analysis parameters (e.g., pCi/g or nCi/m^2 for soil, or pCi/m^3 for air). The basic MDA for plutonium analysis by alpha spectroscopy is based on the amount of plutonium present on the electroplated sample and the count time. Inclusion of the chemical yield and sample size results in secondary MDA's.

Another approach for evaluating the MDA is to consider results of samples that contain essentially no plutonium. Table 17 from Krey and Hardy (1970) presents results from two samples, one collected prior to 1945 and the second collected from a depth of 90 cm in 1970. The analyses were performed on 100-gram samples and the counting errors are only one standard deviation. Thus, the minimum numbers 0.0001 to 0.0003 dpm per gram relate to 10 to 30 fCi per sample (e.g., 0.0001 dpm/g x 10^3 fCi/2.22 dpm x 100 g/sample x 2 sigma = 10 fCi per sample).

The results for the Woodcliff Lake sample are surprisingly high. Krey and Hardy note the probable cause as contamination, either during collection or analysis. Two of the TLW values are noted as suspect.

TABLE 17. PLUTONIUM IN BLANK AND LOW-LEVEL SAMPLES
(From Krey and Hardy, 1970)

Sample	Laboratory	dpm per gram	
		Plutonium-239	Plutonium-238
Pre-bomb (Collected before 1945)	HASL	0.0003 ± 100%	0.0002 ± 100%
"	IPA	0.0001 ± 100%	0.0001 ± 100%
"	IPA	0.0001 ± 100%	0.0001 ± 100%
"	TLW*	0.0196 ± 7%	0.0054 ± 14%
"	TLW	0.0001 ± 100%	0.0001 ± 100%
Woodcliff Lake, N.J. (Collected below 90 cm in March 1970)	IPA	0.0046 ± 7%	0.0001 ± 100%
	IPA	0.0043 ± 6%	0.0001 ± 100%
"	TLW	0.0071 ± 9%	0.0009 ± 53%
"	TLW*	0.0468 ± 5%	0.0001 ± 100%
"	TLW	0.0055 ± 25%	0.0002 ± 100%

* Suspect value

TABLE 16. SUMMARY OF MDA'S FOR PLUTONIUM IN ENVIRONMENTAL SAMPLES

Investigator	Definition of MDA	Basic MDA fCi/sample	Soil fCi/g	Soil Sample Size (g)	Air fCi/m^3	Air Sample Size (m^3)	Water fCi/l	Water Sample Size (l)	Tissue fCi/g ash	Tissue Sample Size (g/ash)
Denham and Waite (1974) Survey[a]	---	--- ^{238}Pu ^{239}Pu	3 3	(0.03-500) (0.4-30)	10^{-3} 5×10^{-3}	(5×10^{-4}-0.1) (10^{-3}-0.1)	5 10	(0.5-50) (0.5-50)		
Johns (1975)	$\bar{x}\leq2\sigma$	20	20 4	1g 10g[b]						
Poet and Martell (1972)		Only report 1 σ error								
AEC (1973a), Sedlet et al. (ANL)	$\bar{x}\pm2\sigma$	~5(?)			10^{-4}	25-60x10^3	0.1 0.5	45 10		
Robinson et al. (1975)			100	10						
E. Geiger (Eberline Instrument Corporation Verbal 5/7/75)	$\bar{x}\pm2\sigma$	20		10						
Krey and Hardy (1970) (estimated by Bernhardt)		~10-55								
Smith and Black (1975)	$\bar{x}\pm1\sigma$	20								
McDowell et al. (1973)	Sample=Bkgd[c]	140	(liquid scintillation, alpha spectrometry)							
Majors et al. (1974)	$\bar{x}>1\sigma$(?)	20 15,000	 (Gamma spectrometry for ^{241}Am)							
McBryde (McClellan, Verbal, 1975)	$\bar{x}>1\sigma$	0.06-6	(Mass spectrometry with sophisticated and routine chemistry)							
Church(1974) REECo et al.		~300,000	3,000 ^{241}Am in soil	100						

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a. Summary paper of AEC Contractor techniques. Single value is considered typical; numbers in sample size column indicate the range.

b. Present yield on 10-gram samples is only about 50%.

c. Sample countrate equals background countrate.

A possibly unfair conclusion would be that "zero" for these samples ranged from 10 to 55 fCi per sample, assuming the two TLW samples can be excluded, which probably would not be the case for unknown samples.

Robinson et al. (1975) report 50 values for a background sample which should have contained only 0.2 fCi/g of plutonium-238. Their values range from 0 to 765 fCi/g, based on a 10-gram sample (no background subtracted). The standard deviation for a single result is a counting error of 40 fCi/g. Two times the counting error, 80 fCi/g, essentially is equal to the average of the 50 results, 77 fCi/g. Based on their analysis, they picked 100 fCi/g as the minimum reporting value for reliable results. This relates to an MDA of 1000 fCi per sample (100 fCi/g x 10g). The intent of the reported project was to assess plutonium-238 contamination significantly above the background level of 0.2 fCi/g for a 12-in core.

Figure 4 is a histogram of Robinson's et al. data. It can be seen that 20 percent of the values (blank or background) are above the MDA of 100 fCi/g.

The optimum MDA, assuming essentially zero background, 1000-min counts, and ignoring the limitations of the statistical assumptions, is about 10 fCi. Practically, a more reasonable minimum is 20 fCi. The value of 20 fCi relates to about 3×10^{-13} g of plutonium-239 or 1×10^{-15} g of plutonium-238. Malaviya (1975) indicates a theoretical capability for mass spectrometry of 10^{-18} g.

In summary, there are several means of defining the sensitivity of analyses, or minimum detectable activity. The techniques that give the lowest MDA's that are reasonably valid are based on the 2- or 3-sigma counting error. The EMSL-LV technique (Johns, 1965), defines the MDA value as the mean value equal to the two-sigma error. Others sometimes use three times the background counting error, which generally gives results similar to Johns (1975). In most instances when mean sample results are below or equal to the MDA, they are expressed as less than the MDA.

It should be recognized that most less than values are only a 50 percent probability statement. That is, 50 percent of the time the statement is wrong. A reasonable minimum MDA is about 20 fCi per sample; i.e.,the counting error is 100 percent at the 2-sigma or 95 percent confidence level. A more realistic MDA statement , given the limitation of the statistical assumptions, would be less than 20 fCi plus 1- or 2-sigma, i.e., 30 or 40 fCi per sample. These values are in essence per sample planchet, after electroplating. If the chemical (tracer) yield is only 50 percent, the values actually are 40, 60, and 80 fCi per original sample.

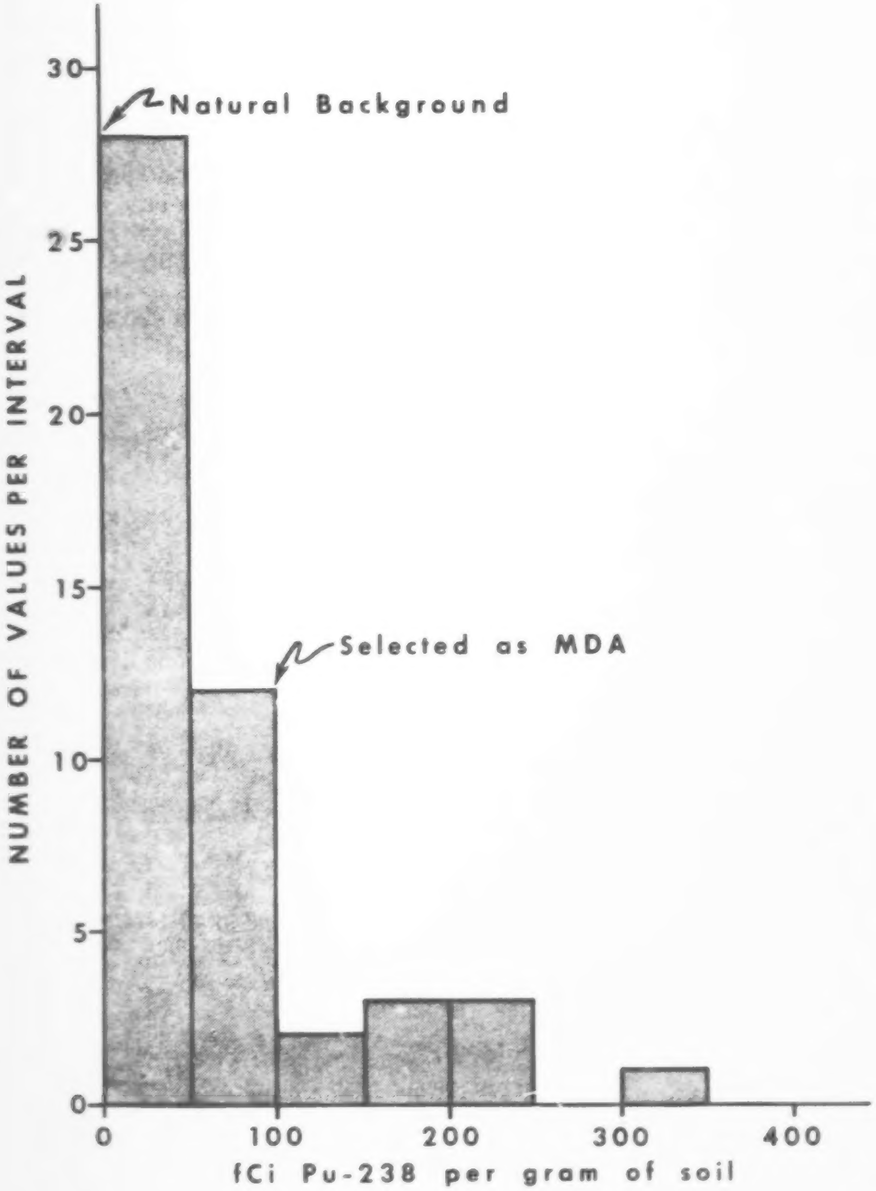

Figure 4. Histogram of blank or background ^{238}Pu soil samples.

Table 18 converts the sample MDA into MDA's for various environmental samples. It is evident from the table that present analytical techniques can detect plutonium at concentrations well below the standards.

SAMPLE TYPES

The chemical and physical characteristics of samples in part determine the dissolution technique for getting the plutonium in solution for analysis, and the steps in the analysis that are necessary to remove elements that interfere with subsequent steps in the analysis, especially electroplating. The various refractory compounds of plutonium, and the generally low solubility of many plutonium compounds, requires emphasis on the complete dissolution of the sample material to assure dissolution of any associated plutonium. If there is residual sample material, there is concern that there may be plutonium in the residual. Sill et al. (1974) and Sill and Hindman (1974) indicate that non-fusion techniques may leave up to 40 percent of refractory plutonium in the undissolved residual.

The refractory nature of plutonium in the sample is related to several factors, including the following:

1. History of the source of the plutonium in the sample and its particle size distribution. For example, Rocky Flats and global fallout plutonium generally are amenable to leaching techniques (Krey and Hardy, 1970), while plutonium from many of the NTS tests appears to be in the form of generally insoluble discrete particles.

2. Sample preparation techniques, such as firing to remove soil organic matter, can produce refractory plutonium (Sill and Hindman, 1974). Sill and Hindman indicate that temperatures of about 700-1000°C produce refractory plutonium.

3. The nature of the sample material, particularly soil samples, can have an impact on the dissolution. Limestone and coral are largely calcium carbonate and can be dissolved rather readily with nitric or hydrochloric acid (AEC, 1973; Wessman et al., 1974; and E. Geiger, Eberline Instruments Corporation, verbal communication, May 6, 1975). The amount of calcium in a limestone or coral soil can produce interferences in a fusion-type technique. Iron oxides also are less prevelent in limestone and coral, resulting in less interference from iron.

4. Most soils are composed of from 50 percent to 80 percent sandstone. Thus, there is a large amount of undissolved residual material from leaching techniques,

TABLE 18. MINIMUM DETECTABLE CONCENTRATION

	SAMPLE VOLUME	UNITS[a]	MINIMUM DETECTABLE CONCENTRATION BASED ON SAMPLE MDA OF		POPULATION (INDIVIDUAL) RPG[a]	RATIO: 20 fCi MDA/RPG
			20 fCi	40 fCi[b]		
AIR SAMPLES						
10 cfm - 1 day	400 m^3	fCi/m^3,x10^{15}uCi/cc	0.050	0.10	60	0.0008
10 cfm - 3 day	1,200 m^3	fCi/m^3,x10^{15}uCi/cc	0.017	0.03	60	0.0003
10 cfm - 7 day	2,800 m^3	fCi/m^3,x10^{15}uCi/cc	0.007	0.014	60	0.00012
40 cfm - 1 day	1,600 m^3	fCi/m^3,x10^{15}uCi/cc	0.013	0.025	60	0.00021
40 cfm - 3 day	4,900 m^3	fCi/m^3,x10^{15}uCi/cc	0.004	0.008	60	0.00007
WATER SAMPLES						
1-liter	1-liter	fCi/lor10^{12}uCi/ml	20	40	5×10^6	4×10^{-6}
5-liter	5-liter	fCi/lor10^{12}uCi/ml	4	8	5×10^6	0.8×10^{-6}
SOIL						
1-gram	1 gram	fCi/g	20	40	------[c]	
10-gram	10 gram		2	4	------	
100-gram	100 gram		0.2	0.40	------	

a. 1fCi/m^3 =10^{-15} uCi/cc. These values are n fCi/m^3 or n x 10^{-15} uCi/cc.

b. An MDA of 40 fCi is the same as the MDA for 20 fCi with a 50% chemical yield. A yield of about 100% has been assumed. The MDA's are for 20 or 40 fCi per original sample quantity.

c. There are no Federal Standards for Pu in soil. Colorado stipulates 2 dpm or about 1 pCi/g. The RPG's are those from 10CFR20, for the most limiting form.

with a potential for retained plutonium. Furthermore, there is the potential for plutonium oxide to occur in a siliceous matrix.

5. Liver and kidney samples present analysis problems analogous to or worse than soils because of the presence of heavy metals, other than plutonium. Due to various interference mechanisms, chemical yields at times are close to zero (J. Mullins, EMSL-LV, verbal communication).

6. In essence, analysis of air samples presents the same difficulties as the analysis of soil samples. The plutonium on air filters is associated with essentially the same material, with possibly a smaller particle size distribution, as the plutonium in soil (e.g., 0.05 pCi/g x 100 $\mu g/m^3$ = 0.005 fCi/m^3, roughly one-tenth of ambient air background). The air sample filtering material may present additional analytical difficulties (e.g., fiberglass air filters are difficult to dissolve and have metals that interfere with the analysis of plutonium).

REVIEW OF ANALYTICAL TECHNIQUES

As in most areas of life, there are few absolute generalizations that can be applied to plutonium analytical techniques. Recognizing this, but also recognizing a need for categorization, plutonium analytical techniques may be divided into three basic techniques for getting the plutonium in solution and four techniques for plutonium quantification.

The techniques for placing the plutonium in solution are:

1. Leaching: The technique generally is related to that of (or represented by) Chu (1971). The basic technique is to leach plutonium from the sample with HNO_3 and HCl. The sample generally is digested for several hours at boiling temperatures. The technique has the advantage of being able to treat large soil samples, nominally 100 g, but up to 1000 g or more. Also, the technique is less likely than other techniques to dissolve interfering elements along with the plutonium. A significant volume of residue remains after the leaching. The technique can be conducted by normal radiochemistry technicians. The disadvantage is the potential for not having dissolved all the plutonium, or having it in an available chemical state.

2. Acid dissolution: This technique can be considered an advanced acid leach. The basic difference is the use of additional HF (the leach technique may use some HF) and the increased digestion and treatment to the point

where essentially the whole sample is placed in solution, with only minimal residue. Hydrofluoric acid has the ability to dissolve silica, and also increases the solubility of refractory oxides, forming fluoride complexes (Sill et al., 1974). The technique generally is amenable to sample sizes of 10 to 15 grams of soil or ash, although the implementation of the technique is easier with 1-g samples. Mullins (EMSL-LV, verbal communication) notes that the treatment of 10-g samples requires the use of professional personnel, or increased supervision of technicians. The increased dissolution of the sample results in increased dissolution of interfering metals. There is an increased probability of dissolving refractory plutonium, but there is still some uncertainty about complete dissolution and chemical availability of the plutonium (Mullins, verbal communication, January, 1975, and Sill and Hindman, 1974). The EMSL-LV method generally is representative of this technique (Johns, 1975).

3. Fusion: Sill (1969) and Sill and Williams (1969) have developed the basic technique of a pyrosulfate fusion for placing uranium and the transuranium elements in solution. The tentative EPA Reference Technique is essentially identical to this method, Hahn et al. (in press). Furthermore, this technique is used to check the efficiency of other techniques (Sill et al., 1974). This method generally is limited to 10-to 15-g samples because of available equipment size limitations. Furthermore, the method requires a high degree of technician proficiency, generally professionals.

Sill et al. (1974) present a summary of the concept of several analytical techniques. The following discussion is based on their review.

Basically, analysis can be broken down into the following phases:

1. Sample dissolution and addition of tracer.
2. Chemical separations to isolate desired elements from interfering elements through precipitation, volitalization, and ion-exchange.
3. Electroplate (or by other means) place sample on planchet or metallic disk (or place in solution for liquid scintillation).
4. Count sample by appropriate technique, such as alpha pulse height analysis.

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4. Count sample by appropriate technique, such as alpha pulse height analysis.

5. Calculate sample activity and estimate analytical error term, based on tracer yield and blank or background count rate.

Church et al. (1974), Majors et al. (1974), and Gilbert and Eberhardt (1974) report data on americium-241 analysis by gamma spectrum analysis. Values for plutonium-239 can be estimated from assumed or calculated plutonium-239/plutonium-241 ratios, based on radiochemistry. Gamma spectrum analysis for americium-241 essentially requires no sample preparation or radiochemistry. The sample is dried and placed in a standard container. Given the relatively low gamma energy (60 keV) and photon abundance, the sensitivity of the method is not adequate for ambient concentrations. The sensitivity is about 100,000 fCi per sample, plus or minus about a factor of five depending on the other gamma emitters present and the counting time. The technique is amenable to samples of roughly 100 grams (e.g., sensitivity roughly 1000 fCi/g or 1 pCi/g). Piltingsrud and Stencel (1973) present similar information for phoswich detectors.

Each of the five analytical steps are discussed in detail below.

Sample Preparation and Dissolution

Sample preparation usually consists of drying the sample at about 100 to 120°C. This normally is the weight basis for reporting results. The difference in weight between air dried (Krey and Hardy, 1970) and oven dried weights may range up to 15 percent (Bliss, EMSL-LV, verbal communication). If there is a significant amount of organic material and roots, the sample is then heated in a muffle furnace to 400°C (Sill et al., 1974) or to 600°C or more; or the material may be burned off with a blow torch, (Bishop et al., 1971). Sill et al. (1974) and Sill and Hindman (1974) express the concern that the high temperatures will increase the refractory nature of the plutonium. This can affect dissolution for silica soils, but apparently does not for coral-type soils.

Many authors recommend sieving the samples subsequent to ball milling them (e.g., Sill et al., 1974 and Krey and Hardy, 1970). Gilbert (verbal presentation at May 1975 NAEG meeting) noted a disparity between sieved and non-sieved aliquots of groups of samples. Gilbert's comments were not conclusive, but indicated a concern for sieving. Possibly a disportionate amount of fines containing plutonium are electrostatically bound to the larger particles.

The following discussion of sample and plutonium dissolution primarily relates to soil samples. However, subsequent to dissolution or combustion of the filter, it also can be related to samples of airborne particulates. The dissolution of ashes from various biological samples is similar.

Most of the techniques are based on dissolving the sample in concentrated hydrochloric and nitric acids. The digesting times and temperatures vary. One of the most significant variations between techniques is the amount and concentration of hydrofloric acid used. Hydrofloric acid is recognized for its ability to dissolve silica, the predominant material in most soils.

Hydrofluoric acid is used to dissolve and break down the silica and soil matrix. The "dissolution" versus leaching processes call for an excess of HF. The leaching processes use little, if any, HF. The HF also acts as a catalyst for breaking down the plutonium and getting it into ionic form in solution.

Sill et al. (1974) and Sill and Hindman (1974) stress the difficulty and necessity of getting the plutonium into a monomeric, ionic form. Plutonium is prone to forming colloids and complex ions. Thus, dissolution alone is not sufficient--it must be in ionic form. Mullins (EMSL-LV, verbal communication) notes that sometimes the miscellaneous heavy metals in liver or kidney tissue can form complexes with the plutonium tracer, resulting in a zero tracer yield. Emphasis must be placed on insuring that the sample and tracer are in chemical equilibrium; e.g., the same ionic state.

It is important that the tracer be added at the right time. If tracer is added to an empty beaker, it may bind to the beaker. The resulting low yield does not reflect the recovery of sample plutonium. Also, if tracer is added too late in the process, the yield will not reflect plutonium losses prior to the tracer addition. In any case, there is always uncertainty as to whether the tracer truly interacts with the plutonium in the sample. The probability is that the tracer may exhibit a yield higher than that of the sample plutonium. But it is possible that the tracer plutonium may also be lost while the sample plutonium is still tied to the sample, thus indicating a yield lower than that achieved for the sample plutonium.

Sill et al. (1974) recommend a combination potassium fluoride and pyrosulfate fusion subsequent to the previously indicated acid treatment to ensure the complete dissolution of the sample and associated plutonium. They note that sodium carbonate or hydroxide fusions do not guarantee complete dissolution, and that the necessary subsequent steps often result in yields of less than 50 percent to as low as 2 percent.

The anhydrous potassium fluoride fusion (in a platinum dish) is used to insure the complete dissolution of siliceous material. The pyrosulfate fusion is used to insure complete dissolution of nonsiliceous materials, especially high fixed oxides (plutonium) along with the volatilization of hydrogen fluoride and silicon tetrafluoride. Except for a small amount of barium sulfate, the pyrosulfate cake resulting from the fusions can be readily dissolved in dilute HCl.

Sill et al. (1974) recommend that the fusion technique be used to check undissolved residuals from other dissolution techniques, resins, and various laboratory equipment. They emphasize the validity of checking residuals versus relying on tracer yields or duplicate analysis by the fusion technique.

Chemical Separations

Sill et al. (1974) precipitate the alpha emitters (radium through californium) with barium sulfate. The various elements are extracted from the solution through control of valence states and solvent extraction. There are several steps where care must be taken to prevent the hydrolytic precipitation of plutonium, the carry-over of iron or quadrivalent cerium with plutonium, and subsequent electrodeposition interference.

Sill et al. (1974) note that for soil samples, calcium is the worst source of interference for the barium sulfate precipitation, because of its relatively high concentration (≃3%) in most soils. If the calcium present in 10 grams of soil precipitates as calcium sulfate and is filtered off, it probably will carry most of the alpha-emitter ions with it. The acidity of solution can be increased by the addition of HCl, but this affects the barium sulfate precipitation. Apparently, these losses are acceptable for plutonium up to a value of about 5 percent calcium in a 10-gram soil sample. A dissolution of the initial barium sulfate precipitate with reprecipitation is necessary to remove small quantities of calcium and other ions which would interfere with electrodeposition and alpha resolution from the deposited sample.

Sill et al. (1974) note various modifications for recovery of the alpha emitters other than plutonium. The basic method is oriented to plutonium.

Sill et al. (1974) report the activity associated with sample residuals and the various pieces of analytical hardware. This data can be used to assess sources of cross-contamination and critical points where sample activity may be lost.

Talvitie (1971) describes the basic method for ion exchange separation of the elements. The technique emphasizes the separation of iron to prevent interference during electrodeposition of plutonium. Talvitie's method is used by Johns (1975).

Bentley et al. (1971) describe the LASL solvent extraction technique. The plutonium is extracted into di-2-ethylhexyl orthophosphoric acid (MDEPH).

Electrodeposition

Electrodeposition generally is used to produce the uniform, essentially weightless, deposition needed for alpha spectroscopy.

The sample must be essentially infinitely thin to minimize self-absorption, or energy degradation, of the alpha particles. Evaporation of solutions on a hot plate does not produce an adequately uniform deposit (Talvitie, 1972). Several alternative techniques include liquid scintillation counting as described by McDowell et al. (1973), and co-precipitation of plutonium with trace amounts of lanthanum carrier (Lieberman and Moghissi, 1968, and Butler et al., 1971). Mass spectrometry also eliminates the need for electrodeposition, but equipment and personnel requirements generally are beyond the resources of most laboratories. Most laboratories utilize alpha spectroscopy after electrodeposition of the sample. Although electrodeposition entails inherent problems, it generally results in a higher quality alpha spectrum than liquid scintillation or plutonium co-precipitation. These alternate techniques, along with mass spectroscopy, will be discussed at the end of this section.

There are several basic potential problems associated with electrodeposition. One basic problem in all radiochemistry procedures is residual contamination of equipment from prior sample analysis. This is especially true with electrodeposition equipment. Talvitie (1972) describes a technique based on disposable electrodeposition cells to minimize this problem. This process is used by EPA/EMSL (Johns, 1975).

Changes in the electrolyte pH during electrodeposition and various elements, such as iron, interfere with electrodeposition, increase the thickness of the deposit, and result in low and variable yields. Talvitie (1972) describes recovery from 1M ammonium sulfate at pH 2 in a period of about 40 minutes. It is recommended that the iron content be less than 0.1 mg.

Puphal and Olsen (1972) describe recovery from ammonium chloride-ammonium oxalate electrolyte over about 50 minutes. They discuss the use of a chelating agent to reduce the interference of some cations, and fluoride to alleviate the interference from iron, aluminum, thorium, and zirconium. But they noted that the presence of even microgram quantities of rare earths can cause serious interference if fluoride is added.

Sill (verbal, EPA/NERC-LV Workshop, now EMSL-LV, April 3, 1974) notes that using methyl red as a pH indicator prior to electroplating results in the possible formation of plutonium hydroxide. Although the pH is corrected prior to electroplating, the plutonium hydroxide may not dissociate and go back into solution. Thus, Sill recommended using thymol blue as the indicator. Hahn et al. (in press), Johns (1975), AEC (1974), and Sill and Hindman (1974) use thymol blue.

Sill et al. (1974) note that subsequent to reasonable dissolution, electrodeposition is by far the step with the greatest potential for loss of the sample. Electrodeposition of electropositive elements such as the actinides depends on deposition of hydroxides by hydroxyl ions produced electrolytically at the cathode. All metal ions forming insoluble hydroxides may be expected to electrodeposit to some extent, degrading the sample plate and thus the alpha spectra. Furthermore, if precipitates are formed during pH adjustments, the element being determined may coprecipitate more effectively than if it were alone and therefore not be available for electrodeposition. This is especially worrisome with high pH's around 4.8 to 6 (i.e., methyl red) which is the justification for recommending the use of thymol blue (pH 1.2 to 2.8). Sill et al. (1974) recommend using the salmon-pink end point of thymol blue (pH 2.0).

Sample Counting Techniques

There are four basic counting techniques: Alpha counting of solid samples, liquid scintillation counting of alpha particles, gamma counting for americium-241 (estimate of plutonium-239), and mass spectrometry.

Various types of alpha counters can be used for gross alpha counting. Lieberman and Moghissi (1968) propose a plutonium method with separations appropriate for gross alpha counting. But as in all gross counting techniques, there is the potential for error as a result of inadequate separation. Bains (1963) notes that ambient-level samples, purified to the extent of about one net count per hour, often contain sufficient natural activity to affect low level results. Bains concludes that spectrometry is needed for low-level alpha work.

Sill and Hindman (1974) and Hahn et al. (in press) suggest standardizing tracer in 2-π alpha counters prior to standardizing alpha spectrometers. The need for cross checking electrodeposition samples (standardization), due to the uncertainties, with standards made up from solutions evaporated on counting disks is stressed. Alpha spectrometers are only calibrated as a general cross check, because normally sample activity estimates are derived from the observed tracer counts versus the amount added (i.e., yield and counter efficiency are considered in a single parameter).

Due to the degradation of alpha particles in the electroplated source, and the separation distance between sample and counter, alpha spectrometers normally operate at 20-30 percent efficiency (Mullins, verbal, February 1975, and Sill and Olson, 1970). Sill and Olson (1970) and experience at EMSL-LV (Mullins, verbal, February 1975) stress the need to consider potential detector contamination from alpha-active daughter products of the sample activity. The concern for contamination relates to the alpha recoil of nuclides, possibly in connection with the volatility of nuclides. Polonium-210 appears to present the greatest hazard. Preheating the plate prior to counting appears to minimize the problem.

Alpha spectroscopy is only appropriate for analyzing the plutonium isotopes of mass 236, 238, 239, 240, and 242. The isotopes plutonium-236 and -242 normally are not found in the environment in significant quantities, and are used as tracers. The alpha energies of plutonium-239 and 240 are so close together they cannot be distinguished by alpha spectroscopy. Plutonium-241 is a beta emitter, and thus, although it is the plutonium isotope normally present in the environment in the largest curie quantities, it cannot be determined by the normal plutonium quantitation techniques. Plutonium-241 quantities normally are estimated from assumed isotopic ratios, from the estimated ingrowth of its progeny americium-241, or by mass spectroscopy.

McDowell et al. (1973) describe a liquid scintillation method for low-level alpha counting. The method has the advantage that electrodeposition, with the associated problems of various interferences, is excluded. But due to the inherently higher background of the liquid scintillation counter, its normal sensitivity is higher than that for solid state alpha spectroscopy. The increased background of liquid scintillation is partially offset by the increased counting efficiency.

McDowell et al. (1973) indicate an alpha counting efficiency of 100 percent with energy determination capability of ±0.1 MeV. The MDA for Pyrex sample tubes is reported as 1 dpm (0.5 pci-whereas for quartz sample tubes the level is reduced to 0.3 dpm (0.14 pCi). If pulse shape discrimination is used, a value of 0.02 dpm or 10 fCi appears attainable.

The normal system background is reported as 1 cpm. This can be reduced to 0.3 cpm by using quartz sample tubes. Pulse-shape discrimination, which requires sample deoxygenation can reduce the background to 0.01-0.05 cpm.

It appears that the sensitivity or MDA has been set equal to the background. Assuming the sample and background counting times are equal, this is equivalent to an MDA where the two-sigma error is equal to or less than the MDA.

Energy discrimination or resolution is such that plutonium-236 tracer and plutonium-239 can be counted simultaneously. McDowell et al. (1973) indicate that background can be determined simultaneously from adjacent channels (away from actual channels of interest). Although this alleviates the need of separate background determinations, it has the potential error of overlooking separation errors, and background due to reagent or equipment contamination. It also is noted that if uranium is not separated from plutonium, impurities in the scintillator may cause overlap of the uranium-234 and plutonium-239 peaks. The uranium-238 peak can be used to estimate the uranium-234 interference.

McDowell et al. (1973) note that iron and other metals do not interfere with liquid scintillation counting, since electrodeposition, the point of interference, is not necessary. Thus, simpler, less time-consuming separation steps may be used (1 hour versus 10 or more hours), and the uncertainties and potential yield reduction associated with electroplating is eliminated.

McDowell et al. (1973) indicate that even with uranium in 10^8-fold mole excess over plutonium, quantitative separation and recovery can be obtained. In summary, it appears that liquid scintillation counting can be used to quantitate plutonium at ambient concentrations, but the equipment and techniques are more sophisticated than normally available at most laboratories.

Lieberman and Moghissi (1968) and Butler et al. (1971) describe a technique using trace amounts of lanthanum to co-precipitate plutonium. The essentially weightless precipitate is collected on a membrane filter and is amenable to alpha spectroscopy analysis. There is some degradation of the alpha spectrum, but apparently most samples can be quantitated easily. If there is too much mass in the precipitate, it can be dissolved and purified. Robinson et al. (1975) report cross-check results between the EPA laboratory in Montgomery, Alabama* which uses this technique and Mound Laboratory. The results show good reproducibility. The co-precipitation technique apparently has received only limited use, but appears to have definite utility, either for those who do not have electrodeposition capability or who would prefer an alternate technique.

Mass spectrometry (MS) provides isotopic data not available from alpha spectroscopy (AS) (plutonium-240 and -241) and it also has greater potential sensitivity than AS. In essence, it is based on counting the number of atoms of a given mass. Thus, its sensitivity, if converted to pCi/g, is greater for long half-life nuclides than for short half-life nuclides, because more mass is present for a given curie quantity. Mass spectroscopy often is used only to determine isotopic ratios, but if a tracer is used, it can be used to quantitate results. It often is used to supplement alpha spectrometry results.

For the long half-life isotopes of plutonium, MS has the potential for several orders of magnitude sensitivity greater than AS. For the present day optimum state of the art, as practiced by the McClellan Air Force laboratory, the routine sensitivity of MS is about an order of magnitude greater than AS sensitivity.

Mass spectroscopy is based on determing the number of atoms of a given mass number. Thus, just as in AS, chemical separations are necessary to remove interfering elements. These interfering elements may be either elements with isotopes of the mass of interest (e.g., uranium-238 and plutonium-238) or isotopes that can be combined with the MS filaments to provide interfering mass units. Thus, more sophisticated chemistry (not justified for routine samples) can be used to increase the sensitivity by roughly an order of magnitude.

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*Eastern Environmental Radiation Facility (EERF).

The sensitivity of MS for plutonium-238 is less than that for AS. This is because of the short half-life of plutonium-238 and interference from traces of uranium-238. Also, because of the short half-life of plutonium-236, plutonium-242 is the preferred tracer. The present state-of-the-art routine sensitivity for MS is about 10^{-13} g of plutonium (Merrell, Air Force McClellan Central Lab, verbal communication May 1975). This can be reduced to about 10^{-15} g with special chemistry techniques. The value of 10^{-13} g is equivalent to 6 fCi of plutonium-239.

Isotopic ratios determined by MS often can be used to determine the source of environmental contamination. Evaluations by Krey (1976) and Krey et al. (1975) illustrate the utility of isotopic ratios, in conjunction with quantitative results, to distinguish the source of contamination.

Americium-241 can be quantitated by either gamma counting with NaI(Tl) wafers (Majors et al.,1974) or Ge(Li) semiconductor detectors. Quantitation is based on the 60-keV photon. Plutonium-239 may then be estimated based on the plutonium-239/americium-241 ratio determined from radiochemistry analysis of a selected number of samples. The sensitivity of the americium-241 method is dependent on the associated gamma emitters in the sample and the counting time. Brady (REECO, verbal presentation, NAEG, May 1975) indicated a plutonium-239 sensitivity of about 50 pCi/g based on a plutonium-239/americium-241 ratio of ten. This relates to an americium-241 sensitivity of about 500 pCi/g. Brady noted the plutonium/americium numbers agreed within about 50 percent with chemistry numbers. The complications of plutonium-239:241 ratios and americium-241 ingrowth time have to be considered.

Piltingsrud and Stencel (1973) report on an X-ray measurement technique for the low-energy X-rays from plutonium-239 and americium-241. The detector is based on a sandwich of a NaI(Tl) crystal backed by a CsI crystal. The two detectors have different pulse rise times, thus photons interacting with both detectors can be discriminated from low energy photons (X-rays) interacting with the NaI detector. The sensitivity is about 20 pCi/g for 500 g samples - 10,000 pCi per sample (plutonium-239 + americium-241).

The detector does not distinguish between plutonium-239 and americium-241 or other low energy X-ray emitters. However, except for plutonium-238 contamination (normally lower than plutonium-239), most of the X-rays would be from plutonium-239 and americium-241.

Calculation of Sample Activity and Estimation of Analytical Error

The calculations are based on multiplying the measured sample activity by the ratio of the known amount of added tracer to the recovered tracer. The counting errors generally are based on propagation of the normal error based on the observed sample and background counts (Johns, 1975).

There are several potential sources of error (not statistical) associated with the various techniques. These include:

1. Use of plutonium-236 tracer, which has a relatively short (2.85-year) half-life. Thus, the standard tracer solution should be corrected for decay subsequent to calibration, and recalibrated periodically.

   In past years plutonium-236 contained a small amount of plutonium-238 contamination. Thus, any initial calibration error would be compounded with time due to the relative increase of the plutonium-238 fraction, due to plutonium-236 decay. The plutonium-238 contamination must be subtracted from plutonium-238 results for samples traced with plutonium-236. Furthermore, the plutonium-236 tracer solution should be purified periodically to prevent interference from the progeny--uranium-232, thorium-228, and subsequent progeny (Sill, 1974).

2. Americium generally is separated from plutonium prior to analysis. The separation factor generally is several orders of magnitude, so although the americium-241 alpha is similar in energy to the plutonium-238 alpha, there should be little problem. But due to the presence of plutonium-241, americium-241 ingrowth must be considered. Mullins (EMSL-LV, February 1975) notes that samples generally are counted within one month of separation.

   Table 19 indicates various plutonium-238:americium-241 ratios. It is evident that americium-241 ingrowth cannot be ignored completely for normal plutonium isotopic ratios.

3. Enough tracer should be added to produce a small counting error for yield estimates. But there is some uncertainty in the necessary amount due to varying yields. Furthermore, if there is too much plutonium-236, its peak can interfere with the plutonium-239 alpha peak. This can be compensated for by using blank reagent samples, including tracer, for background determinations. Sill (1974) and Johns (1975) suggest about 10 dpm per 10-gram soil sample.

TABLE 19. AMERICIUM-241 INGROWTH INTO PLUTONIUM SAMPLES

Activity Ratio [a] Pu-241:Pu-238	Time After Separation (days)	Ci Am-241 [b] per Gram Pu-241	Activity Ratio Pu-238:Am-241
166	0	0	0
166	30	0.013	51
166	60	0.038	17
166	90	0.065	10
166	120	0.15	4

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[a] Assume plutonium-241 is 0.5% by weight or 89% by activity of environmental plutonium at the time of release. Assume the weight percent has decayed to 0.25% (about 15 years). Assume the plutonium-239: plutonium-238 activity ratio is 35. Thus, per gram of plutonium, there is 110.3 Ci/g x 0.25% = 0.276 Ci of plutonium-241 and 0.0614 Ci Pu-239/g x 95% x 1 Pu-238/35 Pu-239 = 1.67 x 10^{-3} Ci of plutonium-238. (Putzier, 1966; Krey and Hardy, 1970, and Del Prizzo et al., 1970).

[b] Putzier, 1966, Figure 13.

4. The separation of polonium from samples should be considered. The alpha from polonium-208 tracer and polonium-210 may interfere with plutonium-239.

5. The background measurement technique and time interim between background measurements can be a source of error. The background from reagents, glassware, and the tracer should be assessed. The potential for contaminating counters (especially from polonium) in part indicates how often backgrounds should be taken.

   Grouping together of samples of similar activity levels for analysis minimizes the potentials for errors due to contamination.

DISCUSSION AND COMPARISON OF TECHNIQUES

Table 20 summarizes the dissolution techniques used by various organizations and investigators. As indicated in the previous sections, assuming a representative sample is taken for

TABLE 20. SUMMARY OF DISSOLUTION TECHNIQUES

Reference	Sample Type	Dissolution Method			Comment
		Leach	Acid Diss.	Fusion	
Church et al.(1974)	Soil		x		REECO, NTS
Johns(1975)	Soil		x		ESML
Krey & Hardy(1970)	Soil	x			Rocky Flats et al.
Major et al.(1974)	Vegetation		x		NTS checked residual by fusion
Talvitie(1971)	Soil, Air Filters		x		
Silland Hindman(1974)	Soil			x	KF & pyrosulfate fusion
Sill et al.(1974)	Soil			x	KF & pyrosulfate fusion
Hahn (in press)				x	Tentative Reference Method
AEC(1974)	Soil		x		
Toribara et al.(1963)	Biological Samples	x		x	Carbonate & bisulphate fusion
Markussen(1970)	Environmental Samples			x	K pyrosulphate, Thule samples
Chu(1971) HASL tech.	Soil	x			Proposes using HF and HNO_3 on siliceous material
Essington (1973) LASL	Soil		x		Modified HASL/LASL
Bokowski(1971)	Soil		x		Rocky Flats, Dow Chem. Repeats HF-HNO_3 step 5 times
Bains(1963)	Biological Samples		x		Leach plus HF.
AEC(1973)	Coralline Soils	x			Enewetak
Keough and Powers(1970)	Biological Samples		x		
Bentley et al.(1971)	Soil		x		LASL
Lieberman &Moghissi(1968)	Environmental Samples		x	x	Alkali fusion
Corley et al.(1971)	Soil	x			Hanford
Butler et al.(1971)	Soil			x	Study of fusion techniques (after Chu, 1971)
Wessman et al.(1971)	Soil	x	x		
Bishop et al.(1971)	Soil	x		x	May use 1 ml of HF in leach

analysis, the primary analytical concern is dissolution of the sample. Other prime concerns relate to consideration and removal, if possible, of interfering elements and ions (calcium, iron, etc.). This interference is of less concern than dissolution, because generally it is reflected by low tracer yields and is thus accounted for.

Analysis of samples by liquid scintillation counting or mass spectrometry eliminates the need for electrodeposition, the analysis step that has the greatest potential for interference and loss of plutonium (Sill and Hindman, 1974). Liquid scintillation tends to be less sensitive, without using special techniques, than solid-state alpha counting. Thus, although it has potential and possibly should be investigated, it will not receive further consideration in this section.

Mass spectrometry has several virtues for plutonium analysis, including providing information on isotopic ratios and improved sensitivity. But due to its limited use for quantitation of environmental plutonium samples, the high sensitivity for plutonium-238, and the expense for organizations to initiate this type of analysis, it will not receive further consideration. Furthermore, it entails the same concerns about dissolution of the initial sample as alpha spectrometry. Also, it has its own unique problems of separation and removal of interfering substances (iron, uranium, and hydrocarbons).

Sample Size

Sample size considerations, based on analytical sensitivity and the representativeness of the sample have been discussed previously. The analytical sensitivity generally is inversely proportional to the sample size (e.g., sensitivity in pCi/g is 10 times higher for a 1-gram sample than for a 10-gram sample). However, the increased amounts of interfering substances in large samples may decrease the chemical yield and thus the relative benefit of large samples. The discrete or heterogeneous nature of plutonium in samples limits the minimum size for analysis aliquots, depending on the acceptable variability of sample results. This potential variability has been discussed previously, but the actual situation will depend on specific sources of contamination and samples.

Sample Dissolution

A basic aspect of sample analysis is getting the plutonium into solution. This not only applies to soil samples, but to vegetation and biological samples. Butler et al. (1971) report results of leaching techniques on two soil samples, one spiked with plutonium-238 (possibly plutonium-239), and one contaminated by an accidental release of plutonium-239. These results are summarized in Table 21.

TABLE 21. SOIL LEACHING EXPERIMENT
(From Butler, et.al. 1971)

Leach Solution	Sample Activity Based on Fusion Analysis (dpm/g)	Percent of Activity in Leached Fraction (a)
Water	1700--Spiked with ^{238}Pu, heated to 550°C	0
4$\underline{N}$ HCl	1700--Spiked with ^{238}Pu, heated to 550°C	92
12$\underline{N}$ HCl	1700--Spiked with ^{238}Pu, heated to 550°C	92
1$\underline{N}$ HF	1700--Spiked with ^{238}Pu, heated to 550°C	0
28$\underline{N}$ HF	1700--Spiked with ^{238}Pu, heated to 550°C	9
4$\underline{N}$ HCl, 1$\underline{N}$ HF	1700--Spiked with ^{238}Pu, heated to 550°C	43
4$\underline{N}$ HCl	0.57 ± 0.40--soil (b) contaminated with ^{239}Pu, heated to 550°C	39
4$\underline{N}$ HCl, 1$\underline{N}$ HF	0.57 ± 0.40--soil (b) contaminated with ^{239}Pu, heated to 550°C	87
4$\underline{N}$ HCl, 2$\underline{N}$ HF	0.57 ± 0.40--soil (b) contaminated with ^{239}Pu, heated to 550°C	> 100

a. One-gram sample boiled in 10-ml volume of leach solution, and allowed to digest for 1 hour. Results based on average of two samples. The two samples varied by less than about 10% except for the 28$\underline{N}$ HF, in which case they differed by a factor of 2.75.

b. Based on analysis of 21 1-g samples. Leach samples are based on treatment of 20-g samples with 200 ml of solution.

Table 22 indicates a comparision of leaching and fusion results from Bishop et al. (1971) of Mound Laboratory and a result from a cross check between laboratories reported by Sill and Hindman (1974). Table 23 reports data from Sill and Hindman (1974) for several different leaching conditions for plutonium fired at various temperatures.

Chu (1971) reports results for three sets of samples analyzed by the leach technique (HCL/HNO_3) and sodium carbonate fusion for both plutonium-238 and -239 (six results). The ratio of the leach:fusion results varied from 0.74 to 1.46, with four of the values being below one. The mean of the ratio was 1 ± 0.24 (1 sigma). It should be noted that Sill et al. (1974) and Butler et al. (1971) report difficulties (e.g., incomplete recovery) for sodium carbonate fusions.

Essington (1973) reports data for analysis of a soil sample spiked with plutonium (any heat treatment not indicated). The results indicate that the former LASL acid leach technique (10-g sample) only recovered about 64 percent of the plutonium-239,based on the EPA/NERC-LV method (Johns, 1975) and the modified LASL leach procedure (includes HF and $NaHSO_3$).

Majors et al. (1974, p. 107) discuss the solubility of plutonium-239 and americium-241 associated with desert vegetation. It is not certain how the plutonium is bound to the vegetation. Although some may be taken up systemically, the major fraction appears to be particulate material deposited on the vegetation (Romney, verbal presentation, NAEG, May 1975). Thus, the majority of the plutonium on vegetation probably is in the same form as plutonium in soil, although possibly associated with less siliceous material. The fraction of plutonium remaining in vegetation ash after an acid leach is given in Table 24.

The fraction of plutonium removed from soil (apparently also vegetation and probably air) samples by acid leaching is variable. Values from various investigators range from less than 50 percent to 100 percent. The validity of the 100 percent value may be questioned, since it is not based on the analysis of the leach residual. Also, it was based on a sodium carbonate fusion versus the technique of Sill et al. (1974).

In summary, it appears acid leaching may recover only roughly 60 percent of soil-related plutonium, depending on the source term. Acid dissolution, using HF may recover all of the plutonium, but prudence would indicate that samples and/or residuals should be checked by Sill's et al. (1974) pyrosulfate fusion technique.

TABLE 22. LEACHING VERSUS FUSION OF SOIL SAMPLES

Technique	Sample Activity (dpm/g)	Percent Activity Leached From Sample	Percent of Activity Found in Residue
HNO_3 leach of Pu-239 sample heated to 1000°C	35	17	81
(Sill and Hindman, 1974), Bishop et al. (1971).	35	24	78
Pu-233 in soil (a)	0.04 ± 0.008	97.5 ± 18	--
Bishop et al. (1971) (b)	0.17 ± 0.03	114 ± 36	--
Bishop et al. (1971) (b)	1.59 ± 0.31	103 ± 15	--
Bishop et al. (1971) (c)	26 ±22	53 ± 18	∿7
Sill and Hindman (1974)	35	27 (3 determinations)	No HF used

(a) Error based on 8 replicate analyses, 1-sigma error

(b) Error based on 6 replicate analyses, 1-sigma error

(c) Error based on 11 replicate analyses, 1-sigma error

The residual of 8 of the aliquots were checked for plutonium-238. The small amount of material found in the leach residual indicates that the sample activity estimate, 26 dpm/g was biased or incorrect, possibly because of discrete particulate material, and the sample size for fusion; 10 g versus 20 or 50 g for leaching. The analysis of residuals infers the leaching recovery was 93 percent versus 53 percent.

Table 23. Leachability of Plutonium from Standard Soil No.3[a] (from Sill and Hindman,1974)

Heat treatment	Plutonium standard	Acid Soluble		Residue		Total	
		dpm/gram	%	dpm/gram	%	dpm/gram	%
2 hours at 110 °C	High[b]	29.2 ± 0.5	98.0 ± 1.6	0.89 ± 0.04	3.0 ± 0.1	30.1 ± 0.5	101.0 ± 1.6
	Low[b]	0.452 ± 0.018	89.9 ± 3.6	0.024 ± 0.004	4.8 ± 0.8	0.476 ± 0.018	94.7 ± 3.4
1 hour at 700 °C	High[b]	19.0 ± 0.3	63.8 ± 1.0	11.4 ± 0.3	38.3 ± 1.0	30.4 ± 0.4	102.1 ± 1.4
	Low[b]	0.256 ± 0.013	50.9 ± 2.5	0.246 ± 0.012	48.9 ± 2.3	0.502 ± 0.018	99.8 ± 3.5
4 hours at 1000 °C	High[b]	5.8 ± 0.1	19.5 ± 0.3	23.4 ± 0.2	78.5 ± 0.7	29.2 ± 0.3	98.0 ± 0.8
	Low[b]	0.071 ± 0.005	14.1 ± 0.9	0.422 ± 0.013	83.9 ± 2.5	0.493 ± 0.014	98.0 ± 2.7
4 hours at 1000 °C	High[c]	17.6 ± 0.2	59.1 ± 0.7	12.0 ± 0.4	40.3 ± 1.3	29.6 ± 0.5	99.4 ± 1.6
	Low						
4 hours at 1000 °C	High[d]	15.4 ± 0.1	51.7 ± 0.4	14.2 ± 0.3	47.7 ± 1.0	29.6 ± 0.3	99.4 ± 1.1
	Low[d]	0.281 ± 0.015	55.9 ± 2.9	0.224 ± 0.011	44.5 ± 2.1	0.505 ± 0.019	100.4 ± 3.6
4 hours at 1000 °C	High[e]	19.2 ± 0.2	64.4 ± 0.7	9.9 ± 0.2	33.2 ± 0.6	29.1 ± 0.3	97.6 ± 1.0
	High[e]	18.5 ± 0.2	62.1 ± 0.7	10.9 ± 0.2	36.6 ± 0.6	29.4 ± 0.3	98.7 ± 1.0

[a] Calculated values are 29.8 ± 0.1 and 0.503 ± 0.003 dpm/gram of ^{239}Pu for the high and low standards, respectively. [b] Ten grams of soil was boiled for 2.5 hours with 100 ml of aqua regia. [c] Ten grams of soil was simmered in a platinum dish for 2 hours with 95 ml of concentrated nitric acid and 5 ml of 48% hydrofluoric acid. [d] Ten grams of soil was moistened with concentrated nitric acid and evaporated to dryness with 40 ml 48% hydrofluoric acid in about 1 hour. [e] Ten grams of soil heated to near boiling for 16 hours with 100 ml of either 95 to 5 or 50 to 50 of concentrated hydrofluoric acid and 8M nitric acid.

TABLE 24. PLUTONIUM LEFT IN VEGETATION ASH AFTER ACID LEACHES*
(From Majors et al., NVO-142, 1974)

Plutonium in Leach (dpm/g ash)	Plutonium in Residue (dpm/g ash)	Plutonium in Residue (Percent of Total)
118	22	16
47	19	29
151	37	20
44	0	0
63	3	5
231	66	24
354	249	41
69	3	4
54	0	0
174	20	10
284	5	2
326	0	0
355	6.2	2

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* Leached with HNO_3-HCl and H_2O_2.

ANALYTICAL VARIATION AND REPRODUCIBILITY

Gilbert and Eberhart (1974) present data on within lab replicate sample variation. The samples are from the NAEG NTS program. Thus, some of the variation probably is due to the discrete particulate nature of the plutonium in the soil. This data reflects a range in the coefficient of variation (sigma divided by the mean) for replicates of 0.23 to 0.93.

Butler et al. (1971) report plutonium cross-check results from aliquots of five standard soil samples. Three aliquots of each sample generally differed by less than 10 percent. The individual values and their means generally were within 10 percent of the known values. The fusion method, after Sill et al. (1974), was used for analysis of the 5-g samples.

Butler et al. (1971) also report the analysis of 21 one-gram replicates of an environmental sample. The sample was taken near a nuclear facility about one year after an accidental particulate release. The contaminated area had been covered with about 12 inches of fresh dirt during the year prior to sample collection. The sample was dried, muffled at 550°C, and thoroughly mixed prior to taking the one-gram aliquots. The fusion results indicated a range of 0.25 to 1.72 dpm/g with a mean of 0.57 ± 0.40 (1 sigma) dpm/g. As indicated in Table 21, acid dissolution of 20-g samples with 4N HCl and 2N HF actually indicated slightly higher and more uniform results.

Chu (1971) and Krey and Hardy (1970) report interlaboratory results related to the HASL Rocky Flats study. The sample sets include aliquots of two samples which essentially should have been zero and several interlaboratory comparisons of different techniques. These data are given in Table 17.

Bishop et al. (1971) reports seven replicate analyses of a soil sample by the fusion technique. The sample was prepared by Sill, after the methods of Sill and Hindman (1974).

Sill and Hindman (1974) report data on an interlaboratory cross-check of their standard soil. This group of data include a comparison of duplicate analyses from seven laboratories by different techniques.

Data from AEC (1973) for the Enewetak cross-check calibration program include interlaboratory analysis of coral soil. There are five groups of data.

These various sets of data, including similar data from Table 12 are summarized in Table 25.[a] The data include the number of samples, sample size, the mean of the results, $(\bar{x})$, the standard deviation, or error, based on the averaging of the results (S), the coefficient of variation, (CV), (the standard deviation divided by the mean), and the coefficient of variation at the 95 percent confidence level (CL) based on the t-distribution (e.g., multiplied by 3.182 for 3 degrees of freedom). The actual percent analytical error also is presented $(\bar{x}-\mu/\mu)$, that is, the difference of the mean from the standard value divided by the standard. Missing data are indicated by horizontal lines. The data are based on analyses of duplicate samples made up from spiked samples, and analyses of actual environmental samples. The emphasis on data selection was to use data sets illustrating analytical variability versus sampling or aliquoting variability. However, selection of data sets for this intent is admittedly subjective. The data from Bliss (1974) and Gilbert and Eberhardt (1974) probably largely reflect sample inhomogeneity versus analytical variations. The data from Bliss (1974) illustrate the reduction in result variability with the increase in sample size.

The data from Sill and Hindman (1974) come from two sources. The first two entries are from an interlaboratory calibration test using the standard soil. The other entries are from efforts to determine analytical sensitivity and sample homogeneity. The samples are based on various dilutions of the standard soil with uncontaminated soil.

Several observations can be drawn from the data in Table 25. There is a large range in the coefficient of variation (at 95 percent confidence level) in the various sets of data; it ranges from as low as 1 to 2 percent for Sill and Hindman's (1974) evaluation of the variance of analysis of standard soils, to hundreds of percent for duplicate analyses of 1-gram aliquot sizes of soils near NTS or interlaboratory analysis of soils with close to zero plutonium levels (Krey and Hardy, 1970). The nominal minimum 95 percent CV is about 10 percent where values of up to 30 to 40 percent are common.

The counting error reported by the various authors (not shown) generally is much lower than the sample result CV. Although the values were similar for Sill and Hindman's (1974) sample variance studies, the sample averaging CV generally was a factor of two or more greater than the counting CV.

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[a] The actual data sets can be obtained from the respective references or a request to Mr. David Bernhardt, Environmental Protection Agency, Office of Radiation Programs, Las Vegas Facility, P. O. Box 15027, Las Vegas, Nevada 89114.

TABLE 25. SUMMARY OF ANALYTICAL VARIABILITY OR REPRODUCIBILITY

Reference	Analytical Technique	Comments	Plutonium-239 Number of Samples	Plutonium-239 Sample Size (grams)	Plutonium-239 Mean, x̄ (dpm/g)	Plutonium-239 Error, S (dpm/g)	Plutonium-239 Analytical Error, x̄→A (per cent)	Plutonium-239 CV S/x̄ (per cent)	Plutonium-239 CV at 95% CL, St/x̄ (per cent)	Plutonium-238 Number of Samples	Plutonium-238 Sample Size (grams)	Plutonium-238 Mean, x̄ (dpm/g)	Plutonium-238 Error, S (dpm/g)	Plutonium-238 Analytical Error, x̄→A (per cent)	Plutonium-238 CV S/x̄ (per cent)	Plutonium-238 CV at 95% CL, St/x̄ (per cent)
Sill and Hindman (1974)	Fusion	Triplicate analyses by Idaho Falls lab	3	10	35.2	0.12	1.2	0.33	--	3	--	0.55	0.056	5.5	10	43
"	Mixed	Triplicate analyses by 7 labs, 1 excluded	21	0.5-10	34.1	1.19	2.0	3.5	7.3	15	--	1.01	0.44	75	43	92
	Fusion	Analysis by Idaho Falls Lab	6	10	32.6	0.24	0.36	0.74	1.9	6	--	0.51	0.02	0.6	3.2	8.1
"	"	"	9	10	0.64	0.057	5.9	9.0	20.7	--	--	--	--	--	--	--
"	"	"	5	10	29.5	0.11	0.94	0.37	1.0	5	--	0.44	0.026	4.8	5.6	16.4
"	"	"	6	1	29.1	0.51	2.4	1.8	4.5	6	--	0.46	0.070	0.7	15	40
"	"	"	6	10	29.4	0.26	1.7	0.9	2.3	6	--	0.46	0.15	1.1	3.3	8.6
"	"	"	9	10	0.503	0.0088	0.2	1.7	4.0	--	--	--	--	--	--	--
"	"	"	6	1	0.553	0.043	10.0	7.7	19.9	--	--	--	--	--	--	--
Sill (1973)	Fusion	Ambient Soil by Idaho Falls	6	10	0.11	0.005	--	5.02	12.9	--	--	--	--	--	--	--
"	"		4	10	0.057	0.0059	--	10.3	32.8	--	--	--	--	--	--	--
AEC (Enewetak), (1973)	Leach	3-8 interlab analysis of coral soil	5	10-50	17.16	1.57	--	9.2	25.4	--	--	--	--	--	--	--
"	"	"	4	"	0.51	0.062	--	12.1	38.4	--	--	--	--	--	--	--
"	"	"	3	"	0.49	0.047	--	9.9	41.8	--	--	--	--	--	--	--
"	"		5	"	2.09	0.66	--	31.6	87.7	--	--	--	--	--	--	--
"	"		4	"	0.45	0.57	--	12.7	40.4	--	--	--	--	--	--	--
"	"	5 - Lab, standard solution	8	--	1278	39	--	3.1	7.3	--	--	--	--	--	--	--
Gilbert and Eberhardt (1974)	Acid dissolution	Analyzed by LASL	34	--	--	--	--	69	135	--	--	--	--	--	--	--
	"		9	--	--	--	--	81	187	Probably reflect discrete particulate matter and sample inhomogeneity						
"	"		15	--	--	--	--	93	200							
"			15	--	--	--	--	58	174							
"			23	--	--	--	--	58	122							
"			12	--	--	--	--	26	57							
"			5	--	--	--	--	33	97							
Butler et al. (1971)	Fusion	(Analyzed by EPA/EERL)	3	5	15.77	0.15	0.55	0.97	4.2	3	--	0.34	0.055	32	16	69
"	"	Cross check samples	3	5	0.031	0.001	0	3.2	13.9	--	--	--	--	--	--	--
"			3	5	2.43	0.13	8.6	5.1	22.1	--	--	--	--	--	--	--
"			3	5	16.34	0.65	4.8	3.9	17	--	--	--	--	--	--	--
"			3	5	0.50	0.04	5.7	8.1	35	--	--	--	--	--	--	--
Chu (1971)	Leach or Na_2CO_3 Fusion	Interlab Comparison	3	--	342	50	--	15	64	3	--	6.57	0.65	--	10	13
		of Leach & HF Dissolution	3	--	1612	15	--	1	4	3	--	33.6	3.2	--	9.4	41
"		and Na_2CO_3 Fusion	3	--	8.07	2.10	--	26	112	3	--	0.18	0.04	--	22.9	98
"	"		2	--	0.63	0.16	--	26	331	--	--	--	--	--	--	--
"			2	--	1.7	0	--	--	0	2	--	0.23	0.26	--	116	1476
"			4	--	0.42	0.06	--	13.8	44	4	--	0.11	0.11	--	100	318
			4	--	4.5	0.29	--	6.4	20	4	--	0.17	0.12	--	70	223
Bishop et al. (1971)	Fusion	Mound Lab-Soil Std	--	--	--	--	--	--	--	6	1	36.8	2.43	1.1	6.6	17
Krey & Hardy (1970)	Leach	Pre-1985 Sample, 3 Labs	5	--	0.004	0.009	--	215	580	5	--	0.0012	0.0024	--	200	55
		Excludes anom. from above	4	--	0.00015	0.0001	--	67	212	4	--	0.00013	0.00005	--	40	127
		Sample from below 90 cm.	5	--	0.014	0.018	--	136	377	5	--	0.00028	0.00035	--	125	346
		Excludes anomolous result from above	4	--	0.0054	0.0013	--	23	74	--	--	--	--	--	--	--
Sill (1973) see Table [illegible]	Acid dissolution	Aliquots of EPA	18	1	1.995	1.419	--	130	200	Data treatment in Table 10 by log normal. Range of data probably related to discrete particulate nature of Plutonium contamination						
		a single Rielo	10	10	2.326	1.53	--	66	149							
		sample from LLL	4	25	3.325	1.109	--	33	106							
		near NTS LLL	4	100	5.025	1.198	--	24	75							
Robison et al. (1975)		Replicates of Background	--	--	--	--	--	--	--	90	10	0.077	0.123	--	160	320

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Figures 5 and 6 are histograms of ratios of results from the AEC (1973) Enewetak program. The ratios represent the results for samples split between the Air Force McClellan Central Laboratory (MCL) and either the Eberline Instrument Company (EIC) or the Laboratory for Electronics, Environmental Analysis Laboratories Division (LFE).

The histograms of the data indicate that the LFE/MCL ratios (Figure 5) are centered around one. AEC (1973) concluded, based on a log normal treatment of the data (geometric mean of 1.02) that the average was not statistically different from zero (95 percent confidence).

The data in Figure 6 indicate the EIC/MCL data are centered about 0.8. The geometric mean, excluding the lowest value of less than 0.1, is 0.85, and indicates statistically significant bias.

The interlaboratory calibration indicated that the EIC value was 94 percent of the average of the other laboratories and 95 percent of the average of MCL. The LLL:MCL ratio was 0.96. The calibrations of these laboratories may not have all been independent. The intent of this discussion is to indicate the variations, not which laboratories were correct.

Robinson et al. (1975) report data from 20 samples split between Mound Laboratory and EPA/EERF. These data indicated a Mound:EPA average ratio of 0.93 ± 0.12 (1 sigma).

Table 26 contains data extracted from Table 25 which are related primarily to analytical variability. The values have been catagorized by the relative level of activity in the sample. Table 27 includes data that generally are related to both sampling and analytical variability.

The lowest sample value in Table 26 (Krey and Hardy, 1970, 0.00015 pCi/g) indicates the greatest variation. This is indicative of analysis near the MDA. The one-sigma counting error for these results was 100 percent of the mean. Assuming a 100-gram sample and roughly 75 percent tracer yield, the counted sample would have contained about 10 fCi (0.00015 pCi/g x 10^3 fCi/pCi x 100 g x 0.75). This sample should have been zero, since it was collected prior to 1945. The value of slightly above zero may relate to minor sample handling or analytical contamination (data given in Table 17).

The data from Robinson et al. (1975) reflect the variability of low level results and the importance of instrument and reagent blank background. The results are based on gross counts with no background subtraction.

Other than the previously discussed "zero" sample in Table 26, the coefficient of variation values show a limited

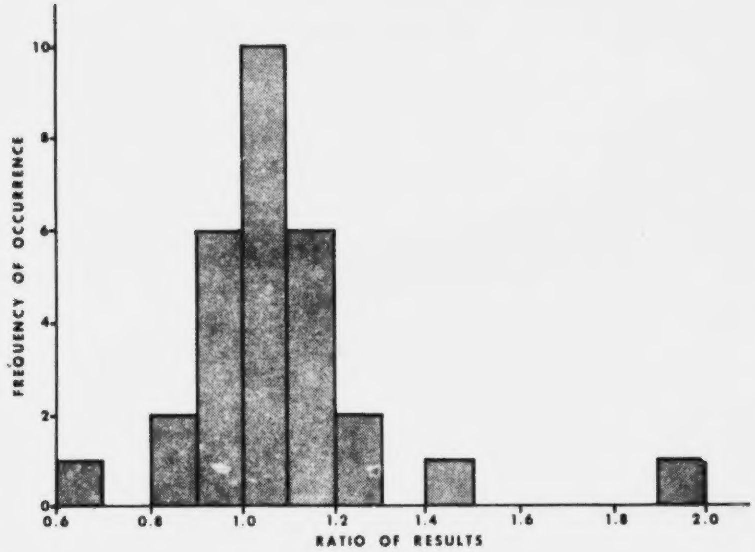

Figure 5. Histogram of ratio of duplicate soil sample results (LFE/MCL) from Enewetak, (Data from AEC,1973))

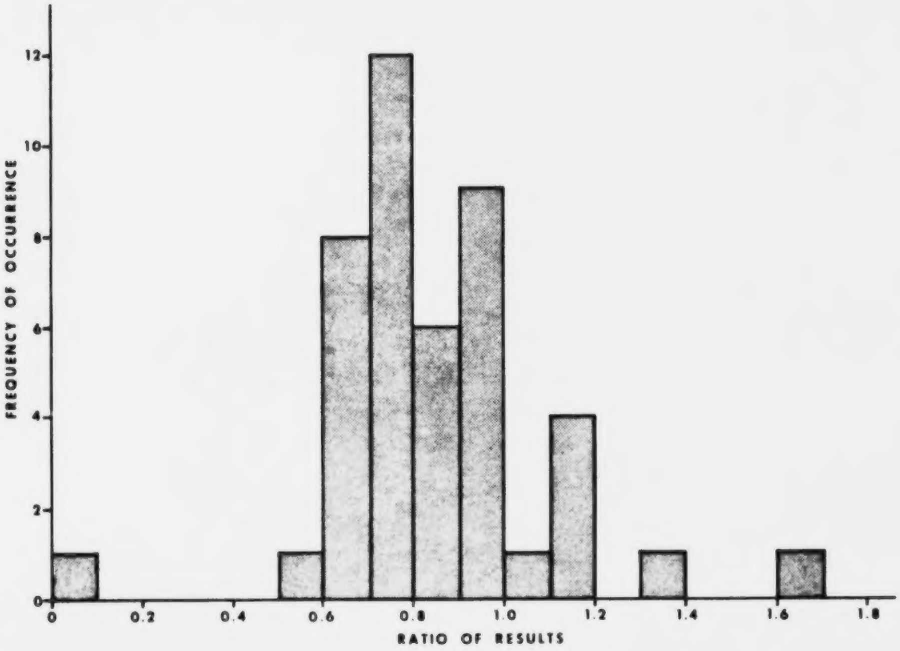

Figure 6. Histogram of ratio of duplicate soil sample results (EIC/MCL) from Enewetak, (Data from AEC,1973)

TABLE 26. VARIABLIITY OF ANALYTICAL RESULTS

		Plutonium-239						Plutonium-238				
Reference	Technique	Number of Samples	Sample Size (g)	Mean (pCi/g)	Difference From True Value (per cent)	CV at 95% CL (per cent)		Number of Samples	Sample Size (g)	(pCi/g)	Difference From True Value (per cent)	CV at 95% CL
Krey and Hardy (1970)	Leach - 3 labs	4	--	0.00015	67	212		4	--	0.00013	40	127 %
Bulter et al. (1971)	Fusion - 1 lab	3	5	0.031	0	14		--				
Sill and Hindman (1974)	Fusion - 1 lab	6	1	0.55	10	7.7		--				
"	Fusion - 1 lab	9	10	0.50	0.2	4.0	11±9%	--				
"	Fusion - 1 lab	9	10	0.64	5.9	21		--				
Robinson et al. (1974)								50	10	0.077	--	320 %
Bulter et al. (1971)	Fusion - 1 lab	3	5	0.50	5.7	35		--				
"	Fusion - 1 lab	3	5	2.43	8.6	22		--				
"	Fusion - 1 lab	3	5	15.77	0.6	4.2		3		0.34	32	69 %
"	Fusion - 1 lab	3	5	16.34	4.8	17		--				
Sill and Hindman (1974)	Fusion - 1 lab	6	1	29.1	2.5	4.5		6		0.46	0.7	40 %
"	Fusion - 1 lab	6	10	29.4	1.7	2.3		6		0.46	1.1	8.6%
"	Fusion - 1 lab	5	10	29.5	0.9	1.0	2±2%	5		0.44	4.8	16 %
"	Fusion - 1 lab	6	10	32.6	0.36	1.9	(exclude	6		0.51	0.6	8.1%
"	Mixed - 7 labs	21	0.5-10	34.1	2.0	7.3	7%)	15		1.01	75	92 %
"	Fusion - 1 lab	3	10	35.2	1.2	0.33		3		0.55	5.5	43 %
Biship et al. (1971)	Fusion - 1 lab	6	1	--				6		36.8	1.1	17 %
AEC (1973) Enewetak	Leach - 5 labs	3	--	1278	3.1	7.3		--				

TABLE 27. VARIABILITY OF ENVIRONMENTAL SOIL SAMPLE RESULTS

			Plutonium-239				Plutonium-238			
Reference	Technique	Type Sample	Number of Samples	Sample Size (g)	Mean (pCi/g)	CV at 95% CL	Number of Samples	Sample Size (g)	Mean (pCi/g)	CV at 95% CL
Krey and Hardy(1970)	Leach-3 labs	Pre-1945	4	--	0.00015	212%	--	--	0.00013	127%
Krey and Hardy(1970)	Leach-3 labs	"(above + 1)	5	--	0.004	598%	--	--	0.0012	555%
Krey and Hardy(1970)	Leach-3 labs	Sample below 90 cm	5	--	0.014	377%	--	--	0.00028	346%
Krey and Hardy(1970)	Leach-3 labs	"(above - 1)	4	--	0.0054	74%	--	--	0.00028	346%
Butler et al.(1971)	Fusion	Amb. Soil	21	--	0.57	144%	--	--		
Robinson et al.(1975)		Background					50	10	0.077	320%
Chu(1971)	Mixed	Amb. Soil	4	--	0.42	44%	--	--	0.11	318%
Chu(1971)	Mixed	Amb. Soil	2	--	0.63	331%	--	--	--	
Sill(1971)	Fusion-1 lab	Ambient Soil	4	10	0.057	33%	--	--		
Sill(1971)	Fusion-1 lab	Ambient Soil	6	10	0.11	13%	--	--		
AEC(1973)Enewetek	Leach-3 or 4 lab	Coral Soil	4	10-50	0.45	40%	--	--		
AEC(1973)Enewetek	Leach-3 or 4 lab	Coral Soil	4	10-50	0.49	42%	--	--		
AEC(1973)Enewetek	Leach-3 or 4 lab	Coral Soil	4	10-50	0.51	38%	--	--		
Bliss(1973)	Accid Dissol	Near NTS	14	1	1.095	280%	Aliquots of same sample,			
Bliss(1973)	Accid Dissol	Near NTS	10	10	2.326	149%	probably reflect discrete particulate			
Bliss(1973)	Accid Dissol	Near NTS	4	25	3.325	106%	non-homogeneous nature of NTS			
Bliss(1973)	Accid Dissol	Near NTS	4	100	5.025	76%	related Pu contamination			
Chu(1971)	Leach or Fusion	Amb. Soil	2	--	1.7	0%	--	--	0.23	1476%
Chu(1971)	Leach or Fusion	Amb. Soil	4	--	4.5	20%	--	--	0.17	223%
AEC(1973)Enewetah	Leach 3 or 4 lab	Coral Soil	5	10-50	2.09	89%	--	--		
Chu(1971)	Leach or Fusion	Amb. Soil	3	--	8.07	112%	--	--	0.18	98%
AEC(1973)Enewetah	Leach 3 or 4 lab	Coral Soil	5	10-50	17.16	25%	--	--		
Chu(1971)Rocky Flats	Leach or Fusion	Amb. Soil	3	--	342	64%	--	--	6.57	43%
Chu(1971)Rocky Flats	Leach or Fusion	Amb. Soil	3	--	1612	4%	--	--	33.6	41%
Eberhart & Gilbert(1974)	Accid Dissol lab	NTS Soil	34	--	--	135%				
Eberhart & Gilbert(1974)	Accid Dissol lab	NTS Soil	9	--	--	187%	Probably reflect discrete			
Eberhart & Gilbert(1974)	Accid Dissol lab	NTS Soil	15	--	--	200%	particulate nature of			
Eberhart & Gilbert(1974)	Accid Dissol lab	NTS Soil	15	--	--	124%	NTS related Pu contamination			
Eberhart & Gilbert(1974)	Accid Dissol lab	NTS Soil	23	--	--	122%				
Eberhart & Gilbert(1974)	Accid Dissol lab	NTS Soil	12	--	--	57%				
Eberhart & Gilbert(1974)	Accid Dissol lab	NTS Soil	5	--	--	92%				

relationship to relative levels of sample activity. Observing only Sill and Hindman's (1974) data, the values below 1 pCi/g appear to have about five times the variation of the values above 29 pCi/g average of 11 ± 9% versus 2 ± 2% at 1 sigma). The respective geometric means and geometric standard deviations are $\bar{x}$ = 9%, s = 2.3 and $\bar{x}$ = 1.5, s = 2.7 respectively. However, this is a limited amount of data (only two concentration classes) from which to make a conclusion. There are not sufficient results from interlaboratory studies to conclude that they have more variance than intralaboratory studies, although there is an indication of this.

The data indicate more uncertainty in the plutonium-238 results than in the plutonium-239 results. Excluding the "zero" result, the means of the percentage uncertainties for concentrations around 1 pCi/g or less are 37 ± 31 percent for plutonium-238 versus 11 ± 9 percent for plutonium-239.

The first four entries in Table 27 are for the above-mentioned pre-1945 sample, and a sample collected in 1970, at a depth of 90 cm. Both samples were analyzed by three laboratories. In both instances the same laboratory presented results about an order of magnitude above the other laboratory's results. Upon request, the sample was re-analyzed with lower, but still elevated, results. The disparity is the reason for the assessment for both four and five samples.

It is possible that the soil sample from 90 cm was contaminated by natural movement of plutonium. However, Krey and Hardy (1970) note that it is probably more likely that the sample was contaminated during collection and handling. This implies the difficulties of handling and collecting samples of grossly different levels of contamination without minor cross contamination occurring. The associated problems are the basis for the recommendation that samples of various stratified activity levels be collected and analyzed separately. Minor cross contamination from one sample can grossly affect the results of a sample of much lower activity.

SUMMARY AND CONCLUSIONS

This report has considered both field instrumentation and sampling and analyses techniques for assessing environmental plutonium concentrations. The report has centered primarily on soil and air sampling techniques and plutonium-238 and -239 analytical techniques. However, much of the information applies to the transuranic elements in general and to other types of samples.

Field instrument techniques are not sensitive enough to assess the ambient environmental levels (roughly 1 nCi/m^2 or less than 1 pCi/g in soil). The FIDLER's sensitivity is indicated as about 130 nCi/m^2, but the variabilities associated with field work indicate uncertainties at even 200 to 500 nCi/m^2 (roughly 50 pCi/g), and the need for confirmatory radiochemistry analyses. Several refinements can be made in using the FIDLER, but basicially it is a survey instrument, not an instrument for quantitating concentrations.

There are several photon counting techniques that allow direct estimation of americium-241, and to a limited extent, plutonium-239 (X-rays), with associated estimates of plutonium-239. The general sensitivities range roughly from 1 pCi/g for americium-241 to 20 pCi/g for plutonium-239.

There are six basic sources of error or variation in relation to plutonium and other transuranic analysis of environmental samples. These are sampling technique (soil), sample size, sample dissolution, inadequate chemical equilibrium between sample plutonium and the tracer, interfering elements, and quantitation of results.

SAMPLING TECHNIQUE (SOIL)

Items to be considered in sampling programs include:

1. Sample representative of stated conditions; i.e., stated depth and area for soil samples. The area sampled should be sufficient to account for minor inhomogeneity.

2. Sample of pertinent depth; i.e., adequate depth to measure total inventory (if that is the objective) and appropriately limited depth to prevent unnecessary

dilution of contaminated layer for deposition or resuspension studies.

3. Generally, it is recommended that samples should represent an area of about 1000 cm² (1 ft²). The variance associated with this or smaller areas has not been quantitated, and would be source-dependent. Sampling errors for a sample of 1-cm depth or less are estimated to be up to 50 to 100 percent. The sampling error for a 5-cm depth (100 cm²) are estimated to be limited to about 20 percent. The estimate of 20 percent is based on soil mechanics theory (Terzaghi and Peck, 1968) and a ORP-LVF field experiment.

SAMPLE SIZE

The potential for plutonium contamination to exist as discrete particles results in a potential variation in sample results of up to several orders of magnitude (roughly 95 percent C.L.) depending on the sample size analyzed and the particle size of the plutonium contamination. The ratio of the upper and lower limits, at the 95 percent confidence level, for 1-gram aliquots of samples is roughly a factor of 10 or more, based on a log-normal distribution (see Table 11). It appears this ratio may be reducible to about 2 (Sill, 1971 data, Table 9) by using 10-gram samples. The ratio is reduced further, at least for less homogeneous samples, by using 25-gram and 100-gram samples.

Michels (1971) evaluated two groups of data for the Rocky Flats, Colorado area. Using a log-normal distribution, he divided the data of Krey and Hardy (1970) into two distributions. One, for global fallout, had a geometric mean of about 2 nCi/m²; the other, generally relatable to Rocky Flats contamination, had a geometric mean of about 15 nCi/m². He notes that the data of Poet and Martell (1972) range somewhat lower (units of nCi/m²) than those of Krey and Hardy. This probably is due to the more shallow sample depth, 1 cm, versus 20 cm for Krey and Hardy (1970). Furthermore, the data cannot be split reasonably into the two distributions, possibly because of the increased variance associated with shallow sample depth and small sample aliquot size (10-g versus 100-g for Krey and Hardy).

Particle Size Distribution of Plutonium In Soil

Soil samples from Rocky Flats, Colorado, were partitioned into size categories of less than 2 mm, 100 micrometer, and 10 micrometer diameters. The mass fractions based on the soil less than 2 mm in diameter were 43 percent and 20 percent, for the less than 100-micrometer and 10-micrometer (density 1 g/cm³) diameter partitions, respectively. The plutonium-239 concentrations (pCi/g) for the 100-and 10-micrometer fractions were 1.8 and 2.5, respectively, times the concentration in the less than 2 mm fraction. These results are in general agreement with those of other investigators.

SAMPLE DISSOLUTION

Sill et al. (1974) and Sill and Hindman (1974 indicate that non-fusion techniques may leave up to 40 percent of refractory plutonium in the undissolved residual for siliceous soils. Butler et al. (1974) further note that sodium carbonate fusions, etc. are not as successful as Sill's et al. (1974) potassium fluoride and pyrosulfate fusions. Furthermore, it is not sufficient to get plutonium into solution only, but it must also be in the monomeric ionic state. Failure to obtain proper chemical equilibrium (ionic state) between the sample plutonium and the tracer gives invalid results, which may be either high or low.

Although acid leaching is adequate in some instances (Krey and Hardy, 1970, and Chu, 1971), it may recover only up to about 60 percent of the plutonium in siliceous soils. Acid dissolution with HF appears to recover more of the plutonium, but still has a potential for incomplete recovery. It would appear to be prudent to check insoluble residuals and complete samples with Sill's et al. (1974) fusion technique. Hahn et al. (in press) and Bretthauer et al. (1975) have proposed this technique as the tentative EPA standard method.

INTERFERING ELEMENTS

Various elements (e.g., fluorine, calcium, iron, uranium, etc.) can interfere with the various separation techniques and stages in the preparation of actinide samples for counting. It is common, and would appear to be necessary, to use tracers (e.g., plutonium-236 or -242) for radiochemistry determinations (other tracers for other elements). Thus, although all of the sample plutonium may not be recovered, the fraction lost, other than from incomplete dissolution, generally is accounted for. Thus, any inaccuracies result in low (lack of dissolution of sample plutonium) results. However, there are two additional considerations. If the plutonium tracer is placed in an empty beaker, it may bond to the beaker and be partially lost. The sample plutonium would be recovered nominally. Furthermore, some techniques (spills and bubbling or spattering) may result in some loss of tracer prior to dissolution of the sample plutonium.

The second consideration is the effect on analytical sensitivity of low tracer yields. This is difficult to quantitate, but a yield of 10 percent has more potential uncertainty than a yield of 100 percent. Plus there is the increased counting error associated with the lower count rates of low recoveries.

Sill et al. (1974) note that the electrodeposition step is the point of greatest potential plutonium loss (reduced yield) in the procedure for alpha pulse height analysis. This is due partially to the potential for plutonium co-precipitation with other elements or the general formation of insoluble or non-electroplatable plutonium. There is the additional problem of uranium or other elements being included in the electroplating and forming a non-weightless plate, with associated alpha self-absorption. Although liquid scintillation counting and co-precipitation of plutonium with trace amounts of lanthanum present alternatives to electrodeposition, electrodeposition appears to be the technique preferred by most laboratories.

QUANTITATION OF RESULTS

The quantitation of results is done by alpha spectroscopy of an essentially weightless sample or liquid scintillation, or mass spectrometry. All of these techniques require radiochemical treatment prior to final analysis. They each have their unique interference problems. Although mass spectrometry is inherently and, at the present state of the art, more sensitive than alpha spectrometry, there is interference from hydrocarbons, and because of the high specific activity of plutonium-238 and interference from uranium-238, the sensitivity for plutonium-238 is poor. Mass spectrometry has the advantage in that it provides isotopic ratios for plutonium-239,-240, and -241 and thus can often be used to relate contamination to specific sources, even when the plutonium-239 contributions are similar.

There are several means of defining the sensitivity of analyses, or minimum detectable activity. The techniques that give the lowest MDA's that are reasonably valid are based on the two or three-sigma counting error. The NERC-LV technique (Johns, 1965), defines the MDA value as the mean value equal to the two-sigma error. Others, (Eberline) sometimes use three times the background counting error, which generally gives results similar to Johns (1975). In most instances when mean sample results are below or equal to the MDA, they are expressed as less than the MDA.

It should be recognized that most less than values are only a 50 percent probability statement. That is, 50 percent of the time the statement is wrong. A reasonable minimum MDA is about 20 fCi per sample; i.e., the counting error is 100 percent at the 2-sigma or 95 percent confidence level. In essence, these values are per sample planchet, after electroplating. If the chemical (tracer) yield is only 50 percent, the values per original sample are doubled.

Variation of Results

An indication of the variance associated with the analysis of samples and with both sampling and analysis is presented by the data summarized in Table 28. These data are summarized from the presentations in Tables 26 and 27. The variance of results is presented in terms of both normal and log-normal distributions. This is not to imply that the data fit these distributions, rather, they are used as tools to summarize the data.

The data in Table 28 illustrate that the variation of environmental soil sample results is much greater than just the analytical variation. The variance associated with sampling and analysis for samples equal to or less than 1 pCi/g is more than twice that associated with just the analysis of samples. There are mixed groups of data and the categorizations may be subjective, but the majority of the various data sets clearly indicate that sampling and analytical error, or just analytical error, exceed the counting error by several factors. Consideration of the data compiled in Tables 25, 26, and 27 indicate that variances of less than 20 percent are the exception, rather than the rule, even for results significantly above ambient concentrations.

The following points become evident:

1. Analytical results for 10-gram samples at ambient plutonium-239 levels (less than 1 pCi/g) can be expected to have (95 percent confidence) coefficient of variation of about 10 percent plus or minus a factor of two. Plutonium-238 results can be expected to have a coefficient of variation of about 30 percent, plus or minus a factor of two or three.

2. Reasonably homogeneous soil samples (10-gram) can be expected to have a 95 percent confidence level coefficient of variation (CF/95 percent) of about 50 percent plus or minus a factor of up to four (one-sigma).

3. Soil samples characteristic of NTS, presumably with discrete particulate material, appear to be characterized with a coefficient of variance of over 100 percent plus or minus a factor of about two. The size of the sample aliquot affects the variation.

4. Data reported by Bliss (1974) exemplify the decrease in variability of heterogeneous samples with an increase in the sample size that is analyzed. The CF/95 percent decreased from 280 percent to 76 percent for 1-gram and 100-gram samples, respectively. This is between a cube and fourth-root relationship.

5. Plutonium-238 soil sample results at ambient levels indicate extreme variability, although only limited data were available.

It should be recognized that the above conclusions are based on normal and log-normal treatments of the data. No tests have been made concerning the applicability of these treatments. However, the statements are not intended to be statistically-proven hypothesis, rather they are indications of trends and categorizations of the data.

TABLE 28. SUMMARY OF VARIATIONS ASSOCIATED WITH ANALYTICAL RESULTS AND SAMPLING AND ANALYSIS RESULTS

Data Averaged	Average of 95 Percent CL Coefficient of Variation (Percent)			
	Normal Distribution		Log Normal Distribution	
	Average	Standard Error	Geometric Mean	Geometric Standard Deviation
Analytical Results				
1. Plutonium-239, $\leq$ 1pCi/g	49	81	20	4.0
2. Plutonium-239, $\leq$ 1pCi/g	16	12	13	2.3
Kreg & Hardy Excluded				
3. Plutonium-239, $\simeq$ 30 pCi/g	3	3	1.9	3.0
4. Plutonium-238	74	95	39	3.4
Sampling and Analysis Results				
1. Plutonium-239, $\leq$ 1pCi/g	110	110	72	2.8
2. Plutonium-239, Other than NTS	76	86	39	4.1
3. Plutonium-239, NTS	140	64	130	1.6
4. Plutonium-239, Bliss, NTS	150	90	135	1.8
4. Plutonium-239 Gilbert & Eberhardt (1974) NTS	130	50	120	1.5
5. Plutonium-239, all	130	190	62	3.6
6. Plutonium-238	330	440	185	3.1

There does not appear to be adequate in-depth data for a rigorous evaluation of analytical and sample result variability. Data of this type probably can be obtained through specially designed intralaboratory and interlaboratory studies.

The results from Tables 26 and 27 contribute confirmation to the previous conclusions.

The following items summarize some additional pitfalls and concerns that must be considered in evaluating environmental data:

1. Low chemical or tracer yields are indicative of difficulties or interferences in the analysis. Prudence would seem to indicate reduced confidence in low yields (roughly defined as below 50 percent, or especially 20 to 30 percent). Low yields can occur because of loss of tracer prior to dissolution of sample plutonium, etc.

2. Sample aliquoting procedures can result in nonrepresentative results. Lung, liver, kidney, etc. samples are not homogeneous. If sections are taken for analysis (especially pertinent to large bovine organs), care must be taken to take representative fractions.

3. Gonads, lymph, etc. produce very small samples, resulting in limited sensitivity.

4. Soft tissues produce variable ash weights depending on the time and temperature of ashing. Results reported per gram of ash are thus variable. Wet tissue weights also are effected by dehydration, depending on packing techniques.

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APPENDIX A

EMSL
WORKSHOP RECOMMENDATIONS
ON
SAMPLING AND ANALYSIS

Summarized by
Dr. Bernd Kahn
and
E. B. Fowler

WORKSHOP RECOMMENDATIONS ON ANALYTICAL PROCEDURE

Dr. Bernd Kahn   Analysis Report   April 3, 1974

It is my impression that the consensus was as follows:

1. EPA should consider two analytical procedures:

   a. The HSL (Idaho Falls AEC Health Services Laboratory) fusion method.

   b. A total dissolution with HNO_3-HF. (Several versions available, some more promising than others. For example, a Los Alamos Scientific Laboratory method which is also the AEC Regulatory Guide Method. More detailed method descriptions, error evaluations and definitions of limits are available and should be obtained from the different laboratories.)

2. In addition, references should be made in the EPA Reference Method to procedures that have special advantages, for example, for processing large samples or numerous samples. The applicability of using these latter methods should be confirmed by comparison with the above cited reference methods.

3. The proposed reference methods should be tested independently by EPA before recommending them.

4. The 10 gram sample size appears to be appropriate, but required minimum detectable levels should be arrived at by the EPA to determine if the 10 gram samples are indeed sufficiently sensitive.

5. The major contribution to the variability of results is believed to be the occurrence of "hot" particles. It is desirable that studies be undertaken to check the influence of sample size in this variability. Guidance should be presented in the Reference

Method to assure that samples will be sufficiently large to minimize variability for the particle size expected at the location from which the methods will be used.

6. Methods should include thorough discussions of the principles and purposes of each of the procedural steps; guidance for minimizing errors, identifying the sources of the errors and calculating the magnitude of the errors; and specify a quality assurance program, including a program for minimizing cross contamination.

7. The importance in using sufficient plutonium tracer for achieving high precision should be indicated. Both Pu-236 and Pu-242 are satisfactory if they are sufficiently pure.

5/74
EBF

COMPILATION FROM THE EPA APRIL WORKSHOP

SOIL SAMPLING

Discussions relating to soil sampling consisted of four parts: (1) presentation of papers, (2) panel discussion, (3) group discussion to fix objectives, and (4) a synopsis of group conclusions.

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Sampling for two general types of mission for radioisotope measurement were identified:

1. Sampling for low levels of radioisotopes such as that associated with worldwide fallout, specifically for preoperational environmental surveillance or the establishment of a base line prior to the installation of a facility; and

2. Sampling to determine levels of radioisotope dispersal due to release associated with accidental incidents, testing, or routine plant emission.

Although the above two are different in some respects, a basic sampling procedure will apply to both situations. In the above two situations there can be permutations such as an abbreviated survey to locate areas for more intensive sampling in case (1), or in case (2) an abbreviated survey to determine whether a suspected release has occurred and if it has, its possible extent.

Further, in case (1), pre and post operational surveys will be required to determine and document the effect or lack of effect of operations on the environment. Case (2) may require an inventory either immediately after or at some period of months or even years after an incident.

It can be argued that continuous air monitoring is sufficient for industrial plant environs; this may be especially true since the predicted plant of the future is a plant of "zero emission". However, since the soil is an integrator and is relatively stable with respect to air it is a desirable matrix for programs involving extended sampling.

With the above factors in mind, the following recommendations are made relative to the establishment of an on-going soil sampling program. It is recognized that some of the permutations referred to will negate certain recommendations, however, any sampling protocol, even the simplest, should fall within the boundaries set forth herein.

The boundaries which define problems associated with a sampling program are outlined in Fig. 1; the objectives to be met are listed in Fig. 2.

The objective of any sampling method is to obtain a representative sample. The following outline is set forth as a guide to accomplish that objective. In the connotation used here, sample preparation is included as a part of the sampling scheme.

Let us assume an extended sampling program which could entail four phases;

1. pre-operation or base line,
2. operational or environmental surveillance,
3. operational incident or release,
4. post release monitoring and inventory.

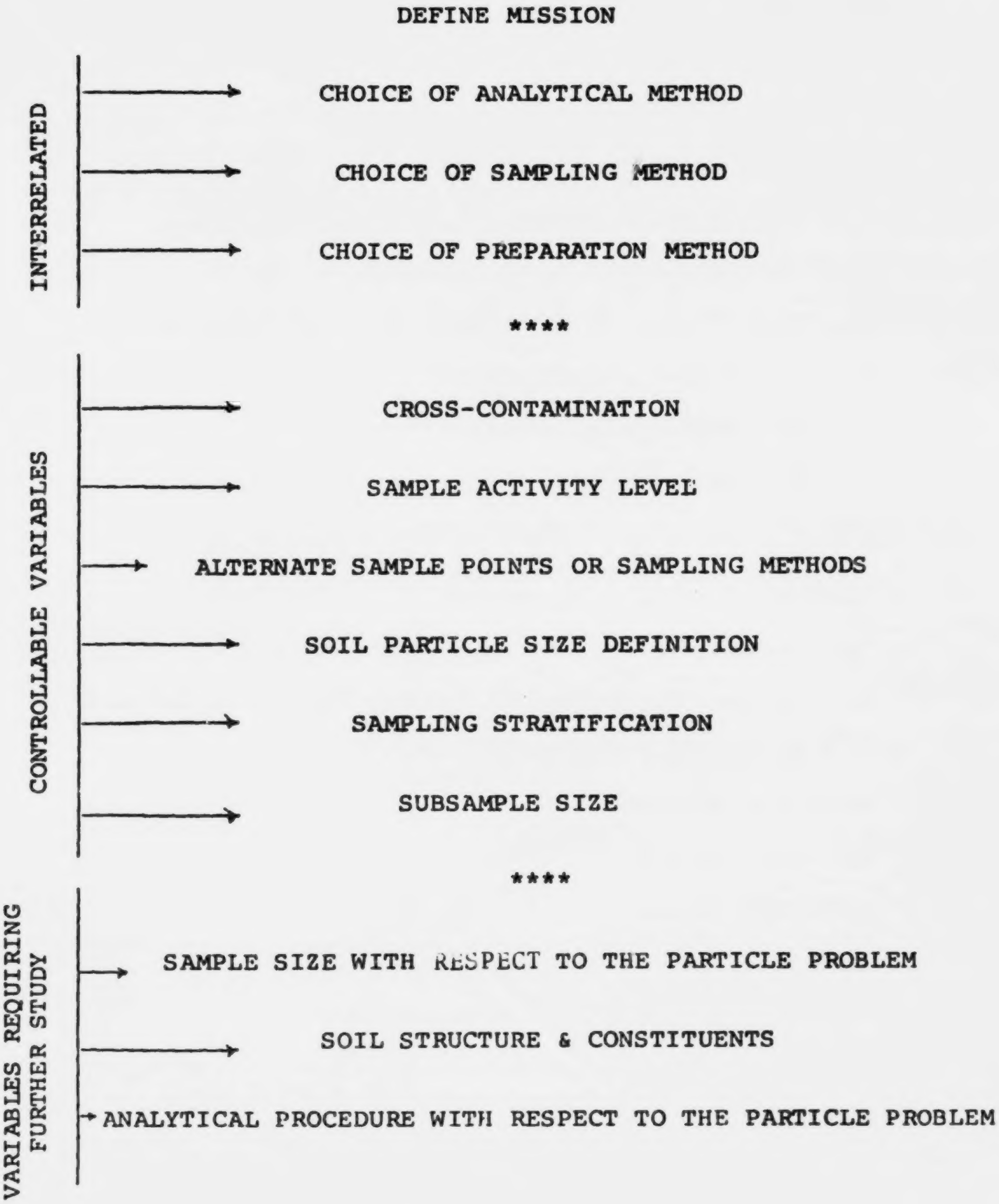
Figure 2

OBJECTIVES

- I. Define Mission
  - A. What is the purpose
    - 1. Pre-op survey
    - 2. Confirm trends
    - 3. Determine inventory (routine operation or accident)
  - B. What nuclides
  - C. What degree of precision is to be considered
    - 1. Number samples/location
    - 2. Number anal./sample
    - 3. Cost
    - 4. Analytical sensitivity
- II. Choice of Analytical Method
  - A. Dependence on sample type and size
  - B. Degree of confidence greater than that defined in mission definition
- III. Sampling Methods
  - A. HASL Method
  - B. NAEG Method
- IV. Choice of Sample Preparation Method
  - A. Dependence on analytical method
  - B. Define excludable material
  - D. Consider need for special treatment

BOUNDARY CONDITIONS

Figure 1


DEFINE MISSION
INTERRELATED
CHOICE OF ANALYTICAL METHOD
CHOICE OF SAMPLING METHOD
CHOICE OF PREPARATION METHOD
****
CONTROLLABLE VARIABLES
CROSS-CONTAMINATION
SAMPLE ACTIVITY LEVEL
ALTERNATE SAMPLE POINTS OR SAMPLING METHODS
SOIL PARTICLE SIZE DEFINITION
SAMPLING STRATIFICATION
SUBSAMPLE SIZE
****
VARIABLES REQUIRING FURTHER STUDY
SAMPLE SIZE WITH RESPECT TO THE PARTICLE PROBLEM
SOIL STRUCTURE & CONSTITUENTS
ANALYTICAL PROCEDURE WITH RESPECT TO THE PARTICLE PROBLEM

A basic requisite to such an extended sampling program relates to the final product, i.e. data reduced to a form that is communicable and meaningful. Statistical advise at all stages of such an extended sampling program is a must. The rationale for statistical advice is two-fold (1) communication of results on a common base,and (2) legalistics of today demand numbers which cannot be refuted.

The sampling program may be nonbiased or biased. A statistically designed program requiring random sampling would be considered nonbiased; an extended sampling program should fall into this category. An abbreviated survey might be biased and could serve an immediate "need to know". It might be acceptable under those conditions or as a starting point or base for a nonbiased extended survey.

Figures 1 and 2 outline the parameters which must be defined in an approach to an acceptable sampling procedure; they will be discussed in detail.

I. Define the Mission

  A. What is the reason for the sampling program?

    1. In the assumed case of an extended sampling program, the reason for sampling will change with time, however, a first requirement will be the establishment of a base line, the pre-operational survey. The survey should be both extensive and intensive in that future trends and conclusions may be based on the initial findings. A well-planned, random sampling scheme will be valuable in the determination

of an initial "inventory". Aside from test, accident, or discharge site, the concentrations of radionuclides found is expected to be low.*

2. A second purpose is that of defining or confirming trends. Any trend will be related to the base line. It is probable that a larger number of samples will be required during early operational experience and that samples will be taken at greater frequency. Complete documentation as in (1) above will prevent a resampling of previous points.

3. A third purpose is that of determining an inventory particularly associated with and after an accidental emission. In case (1) and (2) above, a surface sample only might be required, however for inventory purposes, profile samples will be necessary to assure that the highest practical percentage of a radionuclide has been accounted for.

It is recognized that resuspended soil could have been or may become a part of the soil sample, however, the separate sampling of that fraction is a special case and is not considered in this discussion.

B. What radionuclides are being sought and what is the physical nature of the dispersed material? Plutonium is considered the nuclide of prime importance, however, the sampling scheme is applicable to many radionuclides, including other transuranics as well as uranium. Radionuclides of interest in the future might include the noble gases and tritium, though proposals stated here do not consider such special cases.

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*Drainage areas, low spots, areas of heavy vegetation, and denuded areas should be noted. The basic survey should be as completely documented as possible.

The physical nature of the dispersed material will dictate the sampling design in that particulate material widely dispersed will produce "hot" and "cold" samples whereas an emission of material in a soluble form will result in samples more nearly uniformly distributed in extent of activity. Further, the analytical method of choice may be dictated by the physical nature of the material, e.g. a refractory oxide as opposed to material deposited from solution.

The degree of solubility of the nuclide, hence transport through the soil profile will dictate the need for profile samples and their depths hence the sampling scheme should consider the chemistry of the nuclide being sought as well as the purpose for which samples are taken.

C. What is the acceptable degree of precision?

The acceptable degree of precision is probably a management decision, however, it is related to the defined purpose for sampling. Certainly the need to determine post-incident inventory would require a high degree of precision if a material balance is to be attempted.

For the following discussion, several terms should be defined; it should be pointed out that some definitions may be redundant; they are given here for explanatory reasons:

1. Sample

   That discrete mass removed from a single sampling point.

2. Sampling point

   The defined volume from which a discrete sample is removed.

3. Sampling location

   A volume delineated by a section of a grid, by an isopleth or by other means which may define a supposed commonality (of activity) to the enclosed population.

4. Sampling area.

   The area of experimental interest whose boundaries are defined by the mission. It may be a small area, say 10 x 10 feet associated with a spill or as in the case of worldwide fallout, it is the surface of the earth.

   In considering the degree of precision, the following should be factored into a decision.

   a. The number of samples taken at a location. Certain factors will dictate this number;

they may be knowledge of the problem, previous sampling results, field instrument survey, or others.

b. The number of analyses per sample.
Heterogeneous distribution of particulate matter which varies in size will dictate replication to establish "within sample" variation. Once established, replication on a given percentage of samples should be practiced to confirm the presence or absence of change.

The more nearly homogeneous the sample, the fewer the replications which will be required.

c. Cost.
It is obvious that the greater the number of samples taken and the greater the number of analyses performed, the more precise is the resultant number. Cost will affect the number of samples taken and the number of samples analyzed; a compromise is necessary. The extent of the compromise will be dictated by the mission.

Gilbert (1) has given the following guidance relating the above factors.

$$M_{opt} \doteq \frac{s_a}{s_\mu}\sqrt{\frac{C_1}{C_2}}$$

where: C_1 = cost of taking and preparing one sample from field

C_2 = cost of alalyzing one aliquot

s_μ = standard deviation relating to variation in the field position, and

s_a = standard deviation relating to variation within a given soil sample.

The relationship does consider cost and standard deviation and forms one basis for consideration of the degree of precision.

d. Analytical sensitivity

The adoption of a common analytical method would represent the ideal. In the absence of an ideal situation, the realistic approach is to choose only those methods of analysis which have been shown to yield comparable results and sensitivities. The mission will dictate the sensitivity required in that short cuts in a method may yield results less precise but acceptable to the mission. Such a case might arise when a few samples are taken downwind after a suspected emission as a first check to determine "whether and to what extent". Certainly high analytical sensitivity is desired in the determination of a "most practicable inventory".

II. Choice of the Analytical Method

A. The possible analytical methods of choice will be determined by the group reviewing that problem. However, the choice will be dependent on certain characteristics of the sample. It is also true that characteristics of the sample may dictate minor modifications associated with analyses. As an example, a low organic soil may be digested without pretreatment whereas a high organic soil becomes more amenable to analyses if an ignition step is incorporated to remove organic matter.

The sample size will also relate to the method chosen. The presence of a heterogeneous population of particles dictates replication of analyses or analysis of large samples. The fusion of large samples presents many problems not the least of which is the need to purify from large volumes of salts.

It is also true that the degree of sensitivity desired suffers when very small samples are analyzed.

B. The degree of confidence associated with the analytical method should be higher than that defined for the mission. Although the statement may seem redundant, it is a point often overlooked. Sample should be subjected to the analytical procedure and the "degree of confidence" determined and related to that defined in the mission. Since the sample cannot be changed, the analytical procedure may require modification.

III. Sampling methods

A. Two methods for sampling soils for radioactive constituents have been used with success; these are the HASL method(2) based on the work of Alexander(3) and the NAEG method developed for the sampling of dry, sandy soils. The NAEG method lends itself more readily to true random and profile sampling; it does have the disadvantage of requiring more time per sample than does the HASL method. The mission will determine the method more nearly applicable.

The recently prepared draft guide AEC Regulatory 4.X is also suggested as a reference.

B. Important points related to the sampling of soils for radionuclide content are as follows:

1. As stated, the prime purpose is to obtain a representative and discrete sample hence classical methods, such as conservation auger, do not apply.
2. Cross contamination of samples must be avoided; cross contamination will bias final results, especially profile samples taken for the purpose of determining an inventory.

3. Volume and area of samples must be known precisely as factors in the calculation of overall aerial concentration.

IV. Choice of sample preparation method

Sample preparation is considered a part of sampling in this discussion; it relates to both the sampling method and the analytical method of choice. The cost of analysis (C2, page 3) is markedly effected by preliminary preparation; the purpose of the mission will dictate to some extent the sophistication of the preparation method employed. The best sample is the total sample, however the cost of preparation will dictate screening and/or aliquoting in many cases.

A heterogeneous particle size population will be present in certain types of emissions, e.g. fires or explosions.

Using the method of Leary(4) it has been calculated that a spherical particle of $^{239-240}PuO_2$, 44 microns in diameter, would assay at 86,000 d/m. In an actual analysis of one gram aliquots from the same sample, activities ranging from that level to 6 d/m/g were found.(5)
There is no known state of the art technique which will crush particles of those sizes to a uniform size and distribute them homogeneously throughout the soil matrix.

A prerequisite to sample preparation is the determination of a standard dry weight (105-110°C for 24 hours or to constant weight)(6) on a known vaolume related to a known area.

A. Preparation of the sample is dependent upon the analytical method of choice. The ideal aliquot to be analyzed will represent the entire sample, hence the aliquot taken should not contain stones or pebbles which will drop from the spatula and thus bias the sample. If stones and pebbles are present as such, the dissolution process will be extended and the cost increased. A pulverizing or flouring of the sample is most effective in reducing it to a form most amenable to analyses. However, in this respect samples with detectable activity must be processed in a dry box provided with an adequate air cleaning system; the treatment will produce fines (which have been shown to contain a high percentage of plutonium); the fines will be lost to the filters and the results biased.

A further point relates to cross contamination. A pulverizing mill used to prepare higher activity samples must be dismantled and decontaminated between samples; this is a costly procedure.

B. Definition of Excludable Material

The problems associated with A above can be solved in part by nested or contained mechanical sieving within an enclosure. With a single sieve, two fractions will be obtained---that passing, and that not passing. That passing will comprise the sample for analyses; that not passing is designated excludable material. Excludable in this sense connotes excluded from the primary "to be analyzed" sample. There remains to define the screen size and treatment of the "excludables".

A 10 mesh screen size for preliminary separation is acceptable. Root mat, large organic pieces, stones, pebbles, etc., which will not pass are removed from the sieve and weighed. Root mat and other organic detritus which is a definite part of the soil matrix (i.e., below soil surface level) should be added to the less than fraction and that fraction weighed.

The excludable rocks, stones, etc., may pose a problem; it has been shown that a very small percentage (less than 3%) of total activity is associated with this material(7) and hence may be discarded. However, a confirmation of "negligible percentage" may be desirable in which case the material may be acid washed and the washings added to the less than fraction or analyzed separately; if the washings are added, a second drying and weighing should be performed to obtain final weight of the "less than" fraction and to prepare it for following steps.

It is probable that some samples will contain above ground vegetation. Although this is part of the "collection system", it is not part of the soil system. The mission will define whether the total collector or the soil alone is of importance. In either case, it is recommended that vegetation be removed as a separate sample at ground level. Results of analyses can be weighted and combined if required.

C. The fraction passing 10 mesh is to be blended, mixed or ball milled; ball milling is recommended.

The NAEG procedure employs one (1) gallon paint cans protected by an outer brass sleeve. The protocol designates ball milling to the point where about 90% of the sample will pass a 100 mesh screen. The mission, cost, and analytical procedure will dictate the extent of ball milling. The sample is screened (100 mesh) and the weights of material passing and not passing are recorded. The less than 100 mesh material is the sample used for analysis. Drying at 110°C for 24 hours will generally brittle most material to the extent that it will ball mill properly, however, certain root material will not pulverize. The mission will determine the relative importance of root mat; if important, the organic detritus removed from the 10 mesh screen can be weighed, ignited, and the ash added to the sample being prepared for ball milling. The importance of base stem absorption (collection) has been pointed out by Russel. In certain missions, the effect of this collector should not be ignored.

It is well to maintain a library of prepared samples at least until the results have been compiled, reviewed, and accepted. However, recognize that a "second aliquot" analytical result may be disturbingly different from a former one. One then suspects a particle problem first (evidence to the contrary being absent) and the analytical method second.

D. Need for Special Treatment

A need for special problem or special study samples is not a unique occurrence and is noted here only to alert the reader that on-site decisions may be required to modify either the sampling or preparation procedure or both. The mission as well as physical conditions of the sampling point will determine factors which can be considered for modification. It is strongly urged that the boundaries set forth in Fig. 1 be used to guide the sampling.

V. Addendum

A. Controllable Variables

1. Analytical results are no better than the samples submitted; it is important to control all variables which can be controlled.
    - a. The NAEG sampling protocol presents guidance to minify possible cross-contamination; the added effort required is minimal.
    - b. Sample activity level can be controlled best by instrumental survey in the field to delineate those which are relatively "hot" or "cold" and thus alert the analyst to the aliquot size required for good statistics.

      A second approach involves a screening of samples in the laboratory by means of GeLi scan or other appropriate instrumental survey.

      The GeLi scan for

^{241}Am (60 keV) is especially helpful in the absence of fission products if ^{241}Pu forms a part of the radionuclide population; it is of little value in the presence of significant levels of fission products. Americium-241 x 10 has been used to indicate a possible plutonium concentration. However, the factor of 10 is variable and of questionable value in cases where plutonium concentration is low, hence the technique is limited to certain emission problems. However, the above can in certain conditions guide the analyst as to aliquot size.

c. Alternate Sampling Points - An initial statistical design for random sampling should consider the possibility that a sampling point cannot be used such as extended rock outcrop, hence some alternate random numbers should be available to be chosen should the need arise.

d. Soil Particle Size Definition - The size of soil particles which can be effectively sampled and meaningfully analyzed is limited. This item is closely related to "c." above. A sampling point consisting of one to two inch stones is of questionable value; a second set of random numbers should be available for such events if dictated by the mission.

2. Sampling Stratification

In the case of plutonium distribution (provided ^{241}Pu is present) a FIDLER instrument set to detect the ^{241}Am 60 keV energy peak is of value in delineating stratification and assigning a range of levels to be expected. Such an initial separation assists the analyst in grouping samples of like activity, reduces possibility of serious cross-contamination of samples in the field and guides the statistician in designing the sampling scheme. Other means of stratification may be used such as grass vs areas of brush or dry runs or creek beds vs upland.

3. Subsampling or Aliquot Size

The aliquot size necessary to obtain some relatively constant level of activity per unit volume or per final plate for counting can be determined within reasonable limits by a GeLi scan as previously outlined. The activity per gram in many samples may be so low as to require a volume of soil too large to be accommodated by the analytical procedure and meet the suggestion of constant level of activity per plate. A relatively constant activity per unit volume or per plate simplifies counting (sample changing) and reduces gross cross-contamination possibility when lower level samples follow much higher level samples.

B. Certain Variables Require Further Study; In a Sense, These are Uncontrolled Variables at Present.

It has been pointed out that the distribution of particles relates to sample size. The distribution is one of size of particles as well as aerial distribution. In the cases of an emission or an inventory oriented mission, initial distribution or change in distribution with time are unknown. Investigation to define a representative sample under such conditions will be desirable.

The effect of soil structure and constituents on the representativeness of samples is unknown. Do particles *per se* transport through the soil profile; what is the chemical nature of the radionuclide in the soil constituents on transport, for example, the effect of organic matter on "solubility", chelation, or even insolubilizing of radionuclides? These questions are unanswered.

Such questions relate directly to profile sampling for inventory.

Are the analytical procedures equally effective with respect to all particles and their possible chemical states or forms? What sampling, preparation, and analytical methods apply to glassy material such as trinitite?

Are there conditions under which highly resistant forms (to chemical analyses) are produced -- and thus not accounted for? Tracer recoveries will not provide the answers.

Appendix B

Radionuclide Information

Ref.	Nuclide	Half Life (yrs)	Specific Activity (Ci/g)	Weight % of Nuclide in Weapons Mat.	Predominant α Particles (MeV)	(%)	X-Rays								Gamma Rays							
							10 - 20 keV				20 - 30 keV				20 - 30		keV		55 - 65 keV			
							keV	%	keV	%	keV	%	keV	%	keV	%	keV	%	keV	%	keV	%
(1)	Pu-236	2.85	520																			
(2)		2.85																				
(2)	Pu-238	86		0.04																		
(3)		86			5.50	71.9	13.6	4.60	17	4.31	20.2	0.58					43.5	0.04				
(4)		89.6	16.8		5.50	72			17	13							45	0.034				
(1)		86.4	17.4		5.50	72.2																
(5)			17.34						17-keV band:	10.55												
(3)	Pu-239	24,000			5.16	72.0	13.6	1.74	17.0	1.63	20.2	0.22	band:	3.59	38.6	0.04	46.2	0.001	51.6	0.025	56.8	0.001
(4)		24,400	0.062	94.5	5.14	72.5			17	2.9			band:	2.9	39	0.003			53	0.007		
(1)		24,400			5.16	73.0									39	0.001						
(5)			0.0613						17-keV band:	4.9			band:	4.9								
(2)		24,440		93.34			13.6	1.55	17.2	1.86	20.2	0.39	band:	3.8								
(4)	Pu-240	6,600	0.227	5	5.16	76			17	10							44	0.01				
(1)		6,540			5.16	75.5																
(5)			0.226						17-keV band:	10												
(2)		6,580		6																		
(4)	Pu-241	13.2	113	0.5	4.9	0.004																
(1)		14.8																				
(5)			112.2																			
(2)		13.2		0.58																		
(3)	Am-241	433			5.57	85.3	14	16	17.4	15	20.8	2.0			26.3	3.1	43.4	0.01	59.5	38.4		
(4)		462			5.48	85			17	37					26	2.7	43	0.06	60	37		
(6)									17-keV band:	37.6					26.4	2.5	43.4	0.07	59.6	35.9		
(1)		433															43.4	0.07	59.5	35.3		
(5)			3.22						17-keV band:	37.6												
(2)		433			5.49		14	12	17.8	13	20.8	3	26.3	2.5					59.6	36		
(4)	Pu-242	380,000	0.00391		4.90	76																
(1)		387,000																				
(5)			0.0039																			
(2)		379,000		0.04																		

References:

1. Lederer(In press)
2. Budnitz(1973)
3. Poston(1975)
4. Putzier(1966)
5. Tinney et. al.(1969)
6. Magnusson(1957)

APPENDIX C

TABLE C-1. FREQUENCY DISTRIBUTION TABLE FOR 80 ALIQUOT RESULTS ON REPLICATE SOIL SAMPLES FROM PENOYER VALLEY, NEVADA (from Bliss, 1973)

Interval	Midpoint	Frequency	Cumulative Frequency	Percent Cumulative Frequency
0. - 1.0	0.5	46	46	57.5
1.1 - 2.0	1.5	10	56	70
2.1 - 3.0	2.5	5	61	76.3
3.1 - 4.0	3.5	2	63	78.8
4.1 - 5.0	4.5	3	66	82.5
5.1 - 6.0	5.5	2	68	85
6.1 - 7.0	6.5	3	71	88.8
7.1 - 8.0	7.5	3	74	92.5
8.1 - 9.0	8.5	0	74	92.5
9.1 - 10.0	9.5	1	75	93.8
10.1 - 11.0	10.5	0	75	93.8
11.1 - 12.0	11.5	2	77	96.3
12.1 - 13.0	12.5	2	79	98.8
13.1 - 14.0	13.5	0	79	98.8
14.1 - 15.0	14.5	0	79	98.8
15.1 - 16.0	15.5	0	79	98.8
16.1 - 17.0	16.5	0	79	98.8
17.1 - 18.0	17.5	1	80	100.

Range of Data: 0.15 - 18.0 pCi/g

Interval Width: 1.0 pCi/g

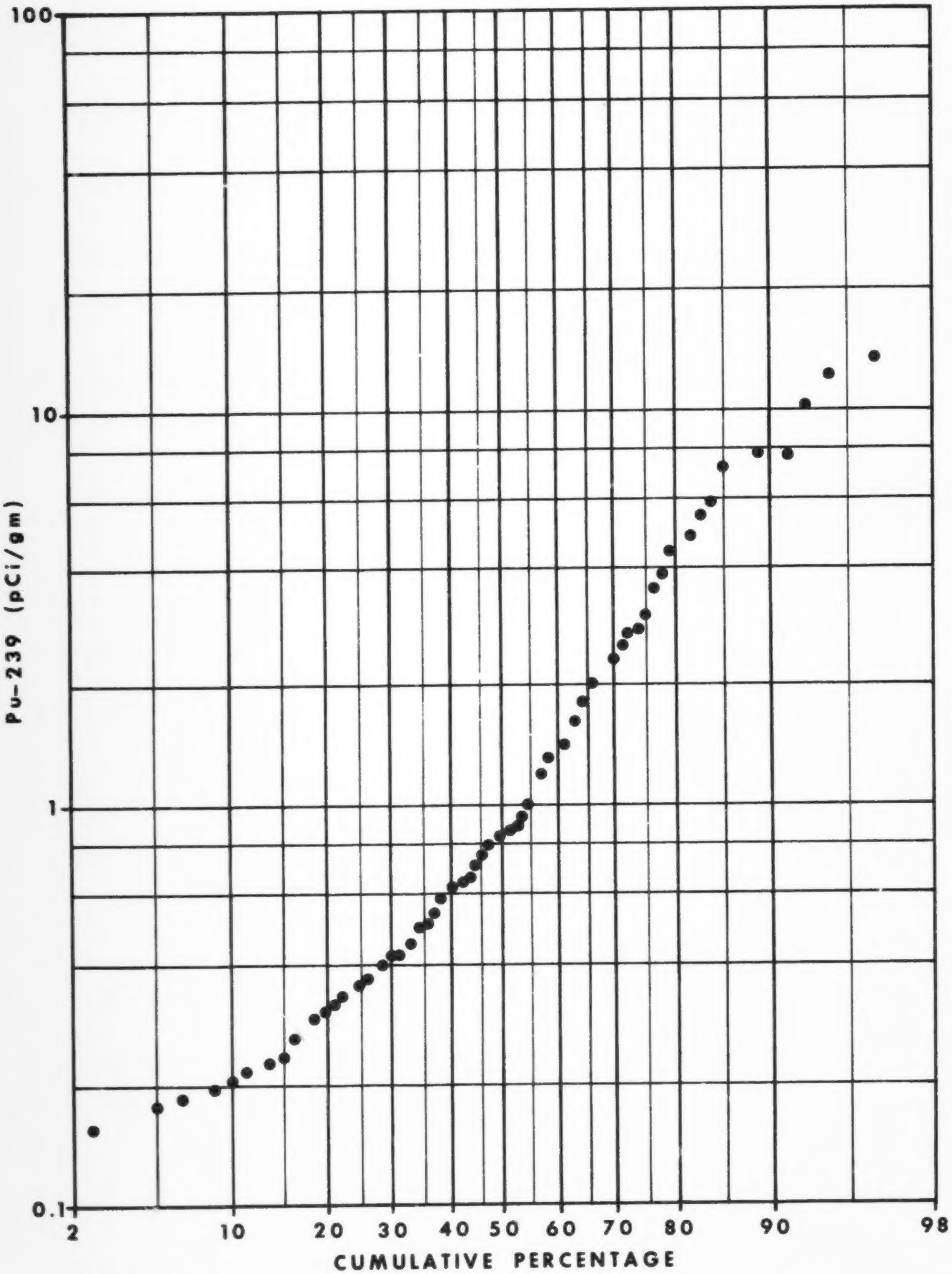

Figure C-1. Probability plot of replicate samples, Penoyer Valley, Nevada.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

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16. ABSTRACT

Information concerning sampling and analysis techniques for plutonium in the environment is presented and evaluated in this report. Consideration is given to available techniques and their applicability to various situations, sensitivities of the techniques, and the validity and reproducibility of results.

Soil is the primary reservoir for plutonium in the environment but inhalation, with the resulting lung dose, is the primary pathway for human exposure. This evaluation is therefore primarily oriented toward sampling and analysis of soil and air, with secondary consideration of other environmental media.

17. KEY WORDS AND DOCUMENT ANALYSIS

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